

# SOME CHALCOGENIDES AS DOPANTS IN SILICON

by

Bengt Skarstam

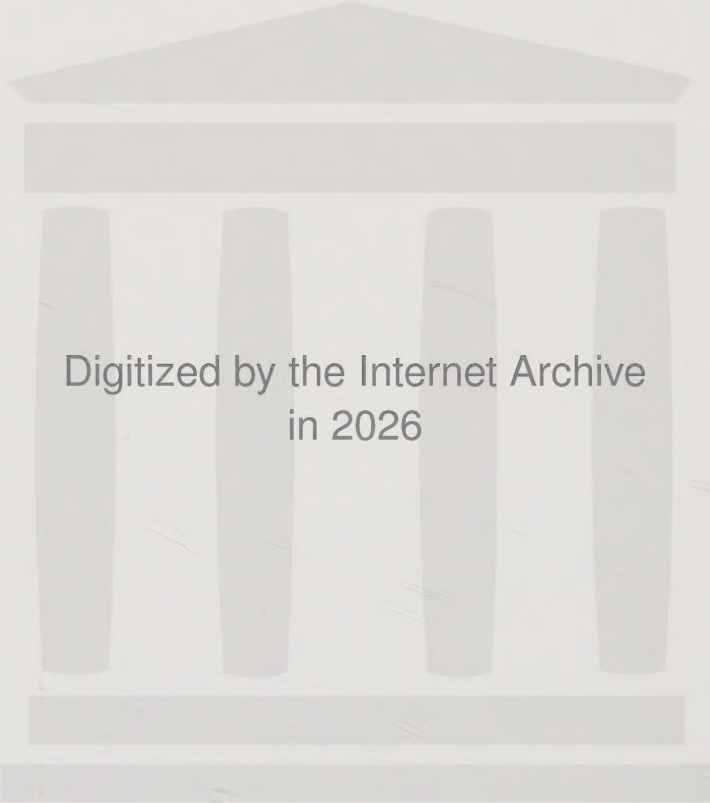
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SOME CHÁLCOGENIDES AS DOPANTS IN SILICON

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| Abstract                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | A4                                     | A5    |
| <p>This work deals with the properties of sulfur or selenium doped silicon. The basic experiments have relied on different kind of junction techniques for the optical and electrical characterisation and in the chemical identification we have used Secondary Ion Mass Spectrometry (SIMS). In selenium doped silicon we found two main energy levels at <math>E_C-0.3</math> eV (B center) and <math>E_C-0.57</math> eV (A center) which should be compared with the energy position of the two main energy levels in sulfur doped silicon at <math>E_C-0.32</math> eV (B center) and <math>E_C-0.59</math> eV (A center) respectively.</p> <p>We have been able to show that the defect centers in Si:Se are due to selenium atoms. Capture of electrons at the B center in both systems have a similar temperature dependence of <math>T^{-3.2}</math> for Si:Se and <math>T^{-3.4}</math> for Si:S. Absolute values of the capture cross section at 100 K are <math>310^{-15} \text{ cm}^2</math> (Si:Se) and <math>210^{-15} \text{ cm}^2</math> (Si:S). The process of capture are explained as capture via an excited state derived from a two stage capture process. This model have been further developed in this thesis.</p> <p>The optical properties for the B centers confirm the thermal data. If it is assumed that the charge of the A centers is equal to two the structure slightly below the ionization limit can be explained as due to excited states. The structure well below the ionization limit, for both systems is explained as due to the multivalley nature of the conduction band.</p> |  |                                        |       |
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Date 15/8 1980











# **SOME CHALCOGENIDES AS DOPANTS IN SILICON**

**by**

**Bengt Skarstam**



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This thesis is based on experimental work performed at the University of Lund, Department of Solid State Physics. The results are presented in the following five papers:

- I. Deep sulfur-related centers in silicon,  
J. Appl. Phys., 51, August (1980)
- II. Electronic properties of selenium doped silicon,  
J. Appl. Phys., 51, 3740 (1980)
- III. Excited states at deep centers in Si:S and Si:Se  
(manuscript)
- IV. Chemical identification of energy levels in Si:Se  
(manuscript)
- V. Capture, emission and recombination at a deep level  
via an excited state (manuscript)

Co-authors: papers I, II, IV and V, E. Janzén. Paper IV, A. Lodding (Gothenburg). Paper V, G. Rees (Plessey, UK) and in papers I-V, H.G. Grimmeiss.







## Some chalcogenides as dopants in silicon

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### Introduction

Changes in the optical and electrical properties of semiconductors owing to the introduction of foreign atoms is since long well established<sup>1,2</sup>). A corresponding knowledge of the local structure of the defect centers responsible for these modified properties is however as yet in its infancy. This is true both experimentally and theoretically but a progress are perceptible inasmuch as new experimental information appears. As far as theoretical treatments are concerned a corresponding new insight has appeared<sup>3,4,5</sup>), which acts as a guide to better models for how a defect structure possessing all the properties experiments reveal is constructed.

In order to get a better understanding of defect centers, more experimental information on suitable systems are needed and this information must be cross-checked by the use of different experimental techniques.

This thesis is a study of the altered electrical and optical properties of sulfur or selenium diffused silicon. Different kinds of techniques, e.g. junction space charge and secondary Ion Mass Spectrometry (SIMS) have been used. In what follows, the ideas and



the techniques used will be presented by first looking at silicon, how to dope it and the identification of electronic centers created in this way. Next, I will comment on the measured parameters e.g. the thermal emission rate, the optical emission rate and the thermal capture rates. Finally the measuring techniques will be explained.

### Silicon

To establish the best possible conditions for these studies we have chosen the semiconductor silicon, since this is a material which can be fabricated to a high degree of reproducibility as far as impurity content and lattice disorder are concerned<sup>6)</sup>. Dislocation free silicon can be grown routinely, but unfortunately new defects; microdefects called swirls appear<sup>7)</sup>. These swirl defects is made electrically inactive by the presence of atomic hydrogen<sup>8)</sup>.

The main residual impurities in silicon are carbon and oxygen, appearing in concentrations of  $10^{17} \text{ cm}^{-3}$  and  $10^{16} - 10^{18} \text{ cm}^{-3}$ , respectively<sup>9)</sup>. Of these, carbon is considered to be electrically inactive whereas oxygen is believed to be responsible for some electrically active centers<sup>10)</sup>. Traces of other chemical elements are also seen in ultra pure silicon<sup>11)</sup>.

Residual impurities in silicon are nowadays believed to play on important role in the formation of the energy levels seen in doped silicon. Being present in the starting material or unintentionally incorporated in the high temperature treatment necessary for the device fabrication, are deleterious, although existing modern silicon technology for manufacturing devices is highly developed. This is of importance when additional doping of the sample are performed.

From the literature, it can be seen that the transport properties of Si are well-accounted for<sup>12,13)</sup> and the infrared properties<sup>14)</sup> including the phonon spectrum<sup>15)</sup>. A crucial quantity involved in many vital parts of the theory of semiconductors is the bandstructure. It can be measured, e.g. at high symmetry points ( $\Gamma$ , X, K etc) and the whole bandstructure is calculated using different methods<sup>16)</sup>. The bandgap of silicon determined in this way is indirect since the valence band maximum and the conduction band minima do not occur at the same point in the  $\bar{k}$  space. The experimentally determined bandgap<sup>17)</sup> is, at 300 K, 1.12 eV and has temperature dependence of  $10^{-4}$  [eV/K]. The softening of lattice modes when an electron is excited from the top of the valence band to the bottom of the conduction band is responsible for this temperature dependence<sup>18)</sup>.

Silicon has six equivalent conduction band minima along the  $\langle 111 \rangle$  directions, and these minima have a profound effect on defects whose ground state are mainly built up by conduction band states<sup>2)</sup>. This multivalley nature splits the sixfold degenerate ground state (predicted by the one valley effective mass approximation) into three energy levels, singly, doubly and triply degenerate, excluding spin. The splitting of the ground state gives additional structure in the photoionization cross section [III].

It is favourable to have this knowledge of the material present when performing investigations of defect-systems in silicon and in connection with the interpretation of experimental data.

A description of the material used and a sample layout is given in II.

### Doping and identification

A common way of introducing foreign atoms into a semiconductor is by diffusion<sup>19)</sup>. This technique has a positive feature compared to ion implantation since it does not introduce any damage in the host crystal which might create additional electrically active defect centers<sup>20)</sup>. Diffusion, a high temperature treatment of the crystal, increases the possibility of introducing unwanted elements since after etching and washing tracer amount of heavy metals on the sample surface<sup>21)</sup> can diffuse into the sample. As mentioned before the substrate always contains a small amount of unavoidable foreign atoms and in addition atoms necessary for giving the sample a specific resistivity, these atoms can also take part in pairing mechanisms together with the intentional dopant<sup>22,23)</sup>. In spite of this, diffusion is a highly suitable technique if control samples are made in a proper way.

It is well known that atoms creating shallow levels in silicon have high solubilities small diffusion coefficients whereas atoms creating deep energy levels have low solubilities and high diffusion coefficients<sup>24)</sup>. When preparing a diffusion experiment with "deep atoms" a starting material of the desired final resistivity and geometrical design must be chosen. Stated in another way, the doping procedure must not disturb the substrate too much. After the diffusion it is necessary to check if the sample has undergone any for the experiment positive changes. By this one has arrived at the feed back step in the doping procedure. The kind of questions to be answered are:

- I: the concentration of the chemical element
- II: the environment around the defect center
- III: the optical, electrical etc properties of the defect center

An answer to these questions is not straight forward since concentration of deep centers in silicon do not exceed  $10^{16} \text{ cm}^{-3}$  (this is in the ppb range and lower). It is possible to have a high concentration but despite that the optical and electrical parameters can be undetectable. Chemical methods can in principle be applicable but its sensitivity can be disturbed by combinations of other elements also present in the sample. These circumstances points to the problem of having more than one method applicable in the cross checking of experimental information.

In this thesis chemical [IV], electrical [I, II] and opto-electrical [III] methods have been used to study the defect system. Unfortunately no methods for determining the local symmetry of the center have been available.

### Energy levels

When a foreign atom is introduced into the host lattice an electronic defect center may appear which have a configuration and symmetry in the crystal reflecting its atomic arrangement and structure. For a long time these centers have been divided into shallow and deep levels. It is always assumed that the binding potential for an electron in a shallow center are much weaker<sup>2,4)</sup> than the corresponding potential for a deep center<sup>25)</sup>. The shallow centers

can be treated in the Effective Mass Theory (EMT) formalism<sup>2)</sup> but this is not normally possible for deep centers. By extending the EMT it has been possible to treat centers originating from atoms isocoric to the host crystal atom<sup>26)</sup>.

The experimental success in determining the properties of shallow levels is due to the existence of excited states and optical and thermal data are in good agreement. The basic reason underlying the successful interpretation of the experimental data is due to the influence of the excited states on the measured parameters<sup>27)</sup>. For deep levels this has scarcely been the case since it has been believed that deep energy states do not possess such character, even if many of the centers studied had a suitable atomic structure. The excited states due to the coulombic part of the potential can be treated in the EMT and among other things depends on the charge of the center, this means that the theoretical treatments is similar for centers with the same charge despite the depth of the ground state. A donor deep or shallow should in fact have something in common, the existence of excited states and as far as sulfur and selenium in silicon are concerned this is certainly so [I, II and III].

Comparing experiment and theory one often encounters the lack of information on the symmetry and the chemical nature of the defect center involved, this favours the assumption of a substitutional center with the symmetry of a host crystal atom. Experiments on sulfur doped silicon have not exclusively established the lattice location and symmetry of a particular defect center<sup>28)</sup> with its energetic position in the forbidden energy gap [I].

From paper I and II it is readily seen that many of the midgap in silicon have the same thermal emission rates. This could be a hint for the existence of an intrinsic favourable energy position which governs the emission rate so as to be the same for all atoms introduced into the silicon lattice. This information modifies one's view of a substitutional high symmetric defect center built up by the incorporated atom alone.

The energy position of centers created by a specific foreign atom in silicon, show a great spread and it is believed that the use of different methods not properly correlated is the cause of this spread. Measurements on deep energy levels must carefully be compared and analysed in the light of all known relevant information for the center under consideration. This is true for results derived from measurements of thermal emission rates when the temperature dependence of the capture cross section is not known. Also of outmost importance is the information on the influence from  $e_n^t$  and  $e_p^t$  on the measured time constant. If excited states, are present they must of course be considered [V, I and II].

To reveal any structure in an optical experiment determining the ionization edge, a high resolution equipment must be available, to ensure the structure not be smeared out. Structures well below the ionization limit are seen in sulfur<sup>29)</sup> [III] and selenium [III] doped silicon and this structure is interpreted as being caused by the multivalley nature of the conduction band mentioned earlier which splits the ground state. From this, it can be inferred that a deep level can actually have shallow levels.

### Thermal emission and capture

The formalism for these parameters is described in papers I and II. The basic equation (Eq. 1. [I]) which relates emission rate ( $e_{n,p}^t$ ) and capture rate ( $\sigma_{n,p}^t$ ) is the detailed balance relationship<sup>30)</sup>.

$$e_{n,p}^t = \sigma_{n,p}^t V_{th} N_{c,v} \exp - (\Delta G_{n,p}/KT).$$

By measurements of  $e_{n,p}^t(T)$  and  $\sigma_{n,p}^t(T)$  it is possible to determine  $\Delta G_{n,p}(T)$ , the energy position involved at least if no disturbances of e.g. the electric field occur.  $\Delta G_{n,p}$  is the change in Gibbs free energy when an electron (hole) is emitted into the band from the energy level considered<sup>31,32)</sup>. This quantity can be divided by standard thermodynamic relations into enthalpy  $\Delta H_{n,p}$  and entropy  $\Delta S_{n,p}$  and written as  $\Delta G_{n,p} = \Delta H_{n,p} - T\Delta S_{n,p}^{tot}$ <sup>33,34)</sup>.

The total change in entropy  $\Delta S_{n,p}^{tot}$  is divided into two parts

I: electronic entropy  $\Delta S_{n,p}^e$

II: vibrational entropy  $\Delta S_{n,p}^v$

all other contributions being neglected<sup>30)</sup> [I,II]. Such a change of formalism alters the common way of specifying energies, in this field, since now the electronic degeneracy is incorporated into the energy concept through an entropy term as earlier pointed out by van Vechten and Thurmond.<sup>35)</sup>

Returning to the entropy  $\Delta S_{n,p}$  a general statement has to be made. The treatment of  $\Delta S_{n,p}^{tot}$  mentioned above requires that the electronic

part must not be coupled to any other entropy contribution e.g. vibrational. Such coupling of these two parts invalids the separation mentioned above<sup>36)</sup>.

Two fundamental quantities in the detailed balance relation-ship are the capture cross section  $\sigma_{n,p}^t$  and the Gibbs free energy since they are theoretical predictable. Experimental information is thus of vital importance for the test and applicability of theoretical models.

The detailed balance relation ship contain, in its present form, the ground state energy only. This picture has to be revised particular in the case of sulfur and selenium doped silicon, since experiments have revealed the presence of energy levels between the ground state and the bandgap. To include their contribution in the emission and capture processes, the detailed balance relationship has to be modified. This can be worked out by incorporating the whole series of excited state in the partition function<sup>34,37)</sup>, which is the basis in the derivation of the detailed balance relation-ship on thermodynamic grounds. Another way, following Gibb et al, is to consider one important excited state and derive expressions for the "two stage capture model"<sup>38)</sup>. A formally more correct treatment, using the picture of Gibb et al is given in V.

The energy for a defect center calculated in this fasion [I,II] and correlated with optical data [III] is as far as we know to day a reliable quantity to be used in comparison with theoretical calculated quantities, especially when the origin of the center is properly known [IV].



### Optical emission

Threshold energies of electronic defect centers are determined by observing transition of the bound carrier from the ground state first to the excited states present and then to the continuum giving the ionization limit. In this way the spectral dependence of the photoionization cross section can be obtained. This quantity has been of considerable interest and a corresponding experimental interest shown in the development of better measuring techniques with high resolution. The experimentalist can measure to a high degree of accuracy whereas the energy calculated does not have the same degree of accuracy since it is influenced by so many parameters and approximations<sup>4)</sup>. Quantities of importance are the impurity wave functions, potential and how to take the real bandstructure into proper account<sup>39,40)</sup>. The local structure of the defect center not to be forgotten.

In these calculations care is only taken to the continuum and higher up in energies, not reflecting the behaviour of the cross section for energies below the ionization limit. Signals in this region are normally seen in spectrum for shallow levels in silicon. In the case of deep impurities however this is seldom seen or resolved. These transition are seen as sharp peaks in the spectrum corresponding to the transition of electrons (holes) from the ground state into an excited state and then up in the conductionband.

We have been able to resolve such structure in the ionization cross section of the deep levels seen in Si:S and Si:Se by optical means [III].

A series of coulombic excited states belonging to a positively charged donor center has an energy distance to the conduction band of only 10 meV to 50 meV depending on the charge of the center when ionized<sup>41)</sup>. An energy state with a binding energy in that range possesses an enormous thermal emission rate (in the temperature interval where measurements are feasible on a silicon diode) which our normal tungsten light sources can never compete with. Light of energy equal to the energy distance between the ground state and the particular energy state can thus transfer the bound electron to the excited state and, due to the high thermal emission rate, this state can be thought of as being virtually empty. Consequently the electron will in fact be in the conduction band thereby giving a contribution to the signal, e.g. capacitance.

Kogan et al discussed this process and called such transitions "photothermal transitions"<sup>42)</sup>, (details are given in III). This method has been a successful tool in the investigation and characterisation of residual impurities in Ge<sup>43)</sup> and for transitions between both the ground state and the excited states as well as for transitions between excited states in In P.<sup>44)</sup>

### Measuring techniques

As seen from the preceding paragraphs a measurements of the carrier traffic is essential since from such experimental data it is possible to determine the binding energies of a defect center. Also, the capture and photoionization crosssections can be compared with the value calculated from theoretical models. Of importance is also the solubility, the electrical active concentration, and the diffusion properties of the foreign atoms introduced into the host crystal.

Together this can give information about the importance of the incorporated atom on the altered properties of the host crystal.

In this thesis emission and capture rates have been determined by measuring the time dependence of the capacitance (voltage) or current originating from processes in the depletion region of a p-n junction. The techniques are described in papers II and III and reviews of junction techniques are given in Ref. 45, 46 and 47. It is always assumed, that the concentration of free holes and electrons in the space charge region is negligible and that the concentrations of deep centers are smaller than those of shallow ones. If, on the other hand, the concentration of deep centers are greater than or equal to the shallow concentration, the techniques normally used have to be modified.

The exponential behavior of a transient is restored by keeping the capacitance constant and looking at the time dependence of the voltage needed to maintain the original capacitance<sup>48,49</sup>). This method must be used with some care since in the junction there are a high electric field and the carrier traffic can be affected by this field. The time varying field thus indeed may disturb the transient. One way of circumvent the disturbance from the time dependent electric field is to use the initial slope technique when analysing the transients [III].

Diffusion profiles of defect system can by electrical means be determined by diffuse the species for such a long time that the interesting part of the profile is not deeper than that which can be reached with reasonable values of reverse bias applied to a junction close

to the surface. This technique are described in IV and make use of the method of keeping the capacitance constant (depth) and scanning the temperature thereby obtaining the concentration of defect centers at that particular depth. By varying the capacitance and repeating the temperature scan for every capacitance value the complete profile is obtained. The concentration profile so obtained must be complemented with an atomic identifying measurement of the main chemical element present in the built-up diffusion front.

A diffusion profile can be measured in different ways, e.g. resistance, neutron activation methods which are based on successive etching.<sup>19)</sup>

A completely different method is SIMS, in which ions sputter off the sample surface and the secondary ions created, are mass analysed in a spectrometer. SIMS is not suitable for all systems since the spectrum can be contaminated with aggregates e.g.,  $O_2$  has the same mass as S.

If a chemical and electrical measurement give similar results it can be anticipated that the diffused specie is responsible for the defect profile and energy level investigated.

If the system studied has two dominating energy levels in the forbidden energy gap, some difficulties can arise since a measurement of emission and capture must be at one level at a time. To fulfil this requirement, it is suitable to use light and/or temperature as selective tools<sup>47)</sup>.

### Summary

The work in this thesis is a study of the properties of how silicon is affected when doped with either sulfur or selenium. The basic experiments have relied on different kind of junction techniques for the electrical and optical characterisation and SIMS<sup>+</sup> in the chemical identification. In selenium doped silicon we found two main energy levels at  $E_C-0,3$  eV (B center) and  $E_C-0.57$  eV (A center) which should be compared to the energy position of the two main energy levels in sulfurdoped silicon at  $E_C-0,32$  eV (B center) and  $E_C-0.59$  eV (A center) respectively. Both levels in sulfur doped silicon have the same concentration this is also the case in selenium doped silicon. We have been able to show that the defect centers in Si:Se are due to selenium atoms. If temperature is varied the energy distance between the conduction band and these levels seems more or less to be constant.

Capture of electrons at the B center in both systems have a similar temperature dependence of  $T^{-3.2}$  for Si:Se and  $T^{-3.4}$  for Si:S (in the temperature range of 100K to 250K). Absolute values at 100K are  $3 \cdot 10^{-15} \text{ cm}^2$  (Si:Se) and  $2 \cdot 10^{-15} \text{ cm}^2$  (Si:S). Analysed as a two step capture process the capture are explained as a cascade capture via an excited state. This model, proposed by Gibb et al are further developed in this thesis. Thermal capture cross sections for the A centers was too large to enable any measurement of the temperature dependence of this quantity.

If we assume the charge of the center to be 1, the optical properties (photoionization cross section of electrons) of the B center show a satisfying agreement between optical and thermal data. The corresponding cross section for the A centers can be understood only if it is

assumed that these centers are doubly charged. This assumption allow us to interpret the structure slightly below the ionization limit as being due to coulomb excited states. A corresponding good agreement between thermal and optical data for the A centers are apparent if a different capture mechanisms are working in Si:S compared to Si:Se. Present in both systems are also energy states well below the ionization limit which we explain as states originating from the multivalley nature of the conduction band.

In a comparison of both systems the overall behaviour is rather the same. But details in the experimental information reveal some significant differences when comparing thermal and optical data.

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## Excited states at deep centers in Si:S and Si:Se.

by

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### Abstract

The spectral distributions of the photoionization cross sections for the dominant sulfur and selenium related donor centers in silicon are presented. The measurements have been performed at different temperatures using junction space charge techniques. The spectra of the electron transitions to the conduction band are best understood in terms of excited states. Two types of excited states are involved, those which are generally referred to as the Rydberg series and those which originate from the multivalley nature of the conduction band. The latter contain sharp peaks with halfwidths of the order of 10 meV for the deeper donor levels and 2 meV for the shallower centers. The energy positions of these peaks are independent of temperature. The assignments of the ground states and the excited states are discussed and the results compared with previous data obtained from thermal measurements in Si:S and Si:Se.

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### I. Introduction

Good insight into the nature of the impurity centers has been achieved at least for Si and Ge when the foreign atoms belong to the groups of the periodic table closest to that of the semiconductor. They introduce localized donor and acceptor levels close to the band edges which are called shallow energy levels. One of the reasons for our good understanding of shallow centers is that they can be described by effective mass theory. This implies that the centers have a hydrogen-like spectrum of levels <sup>1)</sup>. The assignment of these levels and of the ground state has been considerably facilitated by the fact that optical absorption spectra generally exhibit a number of sharp lines <sup>2)</sup>.

Apart from transition metals, published optical spectra of crystal defects with large binding energies generally show a smooth energy dependence without any of the detailed structure which is otherwise characteristic of shallow energy levels. This is valid for both excitation and recombination spectra and has often been considered as an indication for the non-existence of excited states at deep centers <sup>3)</sup>. This lack of information on excited states has severely inhibited the energy assignment of deep centers. "Deep" impurities with binding energies much larger than those of "shallow" ones are often generated by replacing an atom of the host lattice by an atom which does not belong to an adjacent group of the periodic table <sup>4)</sup>. Detailed studies of deep energy

states have shown that both the measurements and their interpretation are often far more difficult in compound materials than in elementary semiconductors due to residual impurities, non-stoichiometry and the formation of complexes. Elementary semiconductors such as silicon are therefore particularly suited for the study of deep energy states. Of the possible deep impurities in silicon, sulfur and other elements from the same row of the periodic table are of particular interest. All of them have the same number of core electrons (isocoric impurities) and, hence, the closest resemblance to the host atom <sup>5)</sup>.

In two recent papers, evidence was given that both sulfur and selenium create two dominant donor levels in silicon <sup>6,7)</sup>. In sulfur doped silicon the deeper donor level has a "thermal activation energy" of 0.59 eV (the A-center) whereas the binding energy of the shallower center (the B-center) is  $E_c - 0.32$  eV <sup>6)</sup>. In Si:Se the corresponding values are 0.52 eV (the A-center) and  $E_c - 0.30$  eV (the B-center), respectively <sup>7)</sup>. The A- and B-centers have about the same concentrations in both Si:S and Si:Se. From a detailed study of electron capture cross sections, it could be shown that the capture of electrons into the sulfur- and selenium-related B-levels is best described in terms of a cascade capture process. Within the framework of this model, the data were not in disagreement with the existence of the excited states first observed in optical spectra of Si:S by Sah et al. <sup>8)</sup> and Ning and Sah <sup>9)</sup>. Although the electron capture cross section of the A-centers was too large to be measured with the equipment available, the similar thermal properties of the A- and B-centers suggested that both centers might have excited states.

Whereas the optical properties of sulfur doped silicon have been the subject of a number of investigations <sup>10-17)</sup>, information on the optical

properties of Si:Se<sup>17-21)</sup> is rather limited. In several of these papers, the A- and B-centers in both Si:S and Si:Se are considered to be two different charge states of a double donor originating from the same substitutional impurity<sup>13)</sup>. We were unable to prove this conclusively<sup>6,7)</sup> although most of our data are not in contradiction with such a model. It has also been suggested that the A-center in Si:S consists of a group of sulfur centers differing only slightly in energy<sup>22)</sup>. While our data support this interpretation indirectly, no direct evidence could be given<sup>7)</sup>.

The existence of excited states at deep energy levels is of vital importance for a better understanding of deep centers not only of capture processes<sup>23)</sup> but also of the electronic structure in general. In this paper, we wish to present data which show that the electron photoionization cross section spectra of the A- and B-centers in Si:S and Si:Se are best understood in terms of excited states. It will be shown that two types of excited states are involved in the spectra: those which are generally referred to as the Rydberg series<sup>4)</sup> and those which originate from the multivalley nature of the conduction band<sup>1)</sup>. Sulfur is an isocoric impurity in silicon, but selenium is not. Since selenium is isovalent to sulfur, a close resemblance of the electronic properties of the two impurities might be expected as in, e.g., the case of arsenic and phosphorous<sup>5)</sup>. However, it will be shown that there are several distinct differences in the optical properties of Si:S and Si:Se.

## II. Experimental details

All measurements were performed on  $p^+n$  junctions doped with either sulfur or selenium (for details see Ref. 6 and Ref. 7). Photoionization

cross sections of electrons were measured using the constant capacitance transient technique<sup>24)</sup>. This technique implies that the capacitance of the diode is kept constant during the measurements. When the occupancy of the deep centers is changed by illuminating with photons of energy  $h\nu$ , the change in voltage  $\Delta V$  needed to keep the capacitance constant is then proportional to the electron occupancy of the center  $n_T$ . If, furthermore, the initial conditions of the measurements are such that all centers are filled with electrons, it is readily shown that under these conditions  $|d\Delta V(t)/dt|_{t=0}$  is proportional to the photoionization cross section  $\sigma_n^0$  (initial slope technique<sup>25)</sup>). In order to check whether or not the capacitance transients are simple exponentials in form, the total transient was monitored for several representative energies of the spectra. In all cases, the transients were of exponential form. The initial conditions for measuring the photoionization cross section of the deep center,  $\sigma_{nA}^0$ , were chosen to be such that the A-center was completely filled with electrons and the B-center empty.

The photoionization cross sections of electrons for the B-center,  $\sigma_{nB}^0$ , were studied at temperatures well below the freeze-out temperature and for energies  $h\nu < E_C - E_A$ , where  $E_A$  is the energy position of the A-center relative to the valence band. In these measurements, care was taken to reduce any disturbance from thermal background radiation.

In the temperature range investigated and for all photon energies smaller than the bandgap  $E_g$ ,  $\sigma_{nA}^0$  for the A-center was found to be much larger than the photoionization cross sections of holes,  $\sigma_{pA}^0$ , in both Si:S and Si:Se (Figs. 1 and 2). The spectra of  $\sigma_{pA}^0$  were therefore obtained from steady state measurements of the photocurrent  $J_R^0$ <sup>26)</sup>. This procedure was checked with the two light source technique<sup>26)</sup>, which gave similar



results. Since  $E_B > E_A > E_C - E_A$ , the photoionization cross section of holes for the B-center,  $\sigma_{pB}^0$ , could not be studied properly due to the high photocurrent caused by the A-center.

Absolute photoionization cross sections were calculated from measured optical emission rates  $e^0$  and photon fluxes  $\phi$  using the relation  $e^0/\phi = \sigma^0$ . Because of the large differences in sensitivity for intrinsic and extrinsic optical excitations, stray light had to be very carefully excluded during the experiments. An incandescent lamp with either a Jarrel Ash double grating monochromator or a Zeiss MM 12 prism double monochromator was therefore used as a light source. Relative intensities were monitored by a thermocouple, absolute values were measured using a pyroelectric detector. Current measurements were performed with a Keithley 616 digital electrometer. For all capacitance measurements a Boonton 72 B capacitance meter was used.

### III. Experimental results

The spectra of  $\sigma_{nB}^0$ ,  $\sigma_{nA}^0$ , and  $\sigma_{pA}^0$  at 80 K are shown in absolute values for both Si:S and Si:Se in Figs. 1 and 2. The corresponding cross sections of the sulfur related centers are in all cases considerably larger than those of the selenium related centers. Furthermore, whereas the ratio of  $\sigma_{nA}^0/\sigma_{pA}^0$  is about 20 at larger photon energies for sulfur, the corresponding value for selenium is about 70. However, it is interesting to see that the curves of  $\sigma_{nA}^0$ ,  $\sigma_{pA}^0$  and  $\sigma_{nB}^0$  are very similar for both sulfur and selenium.

The logarithm of  $\sigma_{nB}^0$  versus photon energy is shown for Si:S at two different temperatures in Fig. 3. The spectra in the energy region between about 0.275 eV and 0.290 eV are difficult to measure because of the presence of water absorption bands. For comparison, we have also

plotted the values of the enthalpy  $\Delta H$  at 0.320 eV (F) and the energy separation of the ground state from the  $2 p_0$  state at 0.302 eV ( $E_2$ ) as obtained from thermal measurements <sup>7)</sup> (Fig. 3). Note that the energy position of the peak at 0.286 eV (T) is independent of temperature.

The data obtained for  $\sigma_{nB}^0$  in selenium doped silicon (Fig. 4) are very similar with those in Si:S. For comparison, we have also plotted the values for the enthalpy  $\Delta H$  at 0.301 eV (F) and the energy separation of the ground state from the  $2 p_0$  state at 0.286 eV ( $E_2$ ) as obtained in previous investigations of the thermal properties of selenium doped silicon <sup>6)</sup>. The energy position of the peak at 0.270 eV is independent of temperature, as in Si:S.

The photoionization cross sections of electrons  $\sigma_{nA}^0$  for the A-center in Si:S were measured at four different temperatures (Fig. 5). The low energy part of the spectra below about 0.54 eV shows a strong temperature dependence and could only be studied for temperatures above 120 K. The arrow at 0.587 eV ( $E_2$ ) indicates the value of the energy separation of the ground state from the lowest state accessible by electron capture as deduced from thermal measurements <sup>7)</sup>. It is readily seen from Fig. 5 that the energy position of the peak at 0.428 eV (T) is independent of temperature implying a temperature independent energy separation for transitions between the ground state and this particular excited state.

Similar measurements of  $\sigma_{nA}^0$  were performed in selenium doped silicon at three temperatures (Fig. 6). Unlike the spectrum of  $\sigma_{nA}^0$  obtained in Si:S at 40 K, the low energy tail of  $\sigma_{nA}^0$  in selenium doped silicon is very steep and no signal could be detected for energies smaller than 0.537 eV. The spectra in the energy region below about 0.53 eV

are strongly temperature dependent and could only be measured for temperatures above 110 K. For comparison, we have also plotted the value of 0.524 eV ( $E_2$ ) for the energy separation of the ground state from the lowest state accessible by electron capture as obtained from thermal investigations of Si:Se<sup>6)</sup>. As in Si:S, the energy position of the peak at 0.426 meV (T) is independent of temperature.

The spectra of the photoionization cross section of holes,  $\sigma_{pA}^0$ , were measured at several different temperatures for the A-centers in both sulfur and selenium doped silicon (Figs. 7 and 8). In both cases, a temperature shift of the low energy part of the spectra is clearly seen. Furthermore, it is interesting to note that the absolute values of the photoionization cross section  $\sigma_{pA}^0$  at higher energies are independent of temperature in both Si:S and Si:Se.

#### IV. Discussion

Comparing previous results obtained from thermal measurements in sulfur and selenium doped silicon<sup>6,7)</sup> with the results presented in this paper, we feel that the spectra of photoionization cross sections can only be understood if it is assumed that both the A- and B-centers have excited states between their ground states and the conduction band. Transitions from the ground state to excited states are internal transitions and are therefore not expected to cause changes in the diode capacitance similar to those caused when the charge carriers are excited into the conduction band. Any capacitance signal observed which involves excited states must therefore originate from a two-step photo-thermal excitation process in which the electron is first excited from the ground state into an excited state by the absorption of a photon and then, further excited into the conduction band by absorbing one or

several phonons. This type of excitation has been discussed in detail by Kogan et al. <sup>27)</sup>. They found that the photo-thermal excitation process is more probable than the simultaneous absorption of a photon and a phonon provided the electron-lattice vibrational interaction is weak. All published data on electron-lattice interactions suggest that this interaction is probably very weak in silicon <sup>26,28)</sup>.

#### IV a. The deeper donor levels (A-centers)

Starting our discussion with the A-centers, it is clear from what has been said earlier that the part of the spectrum involving the excited states must be thermally activated, in agreement with the results presented in Figs. 5 and 6. A more detailed analysis of the  $\sigma_{nA}^0$  spectra shows that two types of excited states are involved in the spectra. First, there are those which are generally referred to as the Rydberg series and which lie rather close to the conduction band. Using effective mass theory, the deepest of these excited states for a donor in silicon should be the  $2 p_0$  state <sup>4)</sup>. Due to possible broadening effects caused by the high electric field in the junction and the closely spaced energy levels of the excited states, it is not to be expected that these states can be resolved in great detail. Instead, it can be anticipated that the optical signal should increase rapidly for photon energies larger than the energy separation between the ground state and the  $2 p_0$  state.

It is readily seen from Fig. 6 that for Si:Se the threshold energy of the spectra taken at lower temperatures is about 0.53 eV, which is very close to the value of 0.524 eV for  $E_2$  obtained from thermal measurements <sup>6)</sup>. Using the arguments of Gibb et al. <sup>29)</sup>, this result could imply that as

for the B-centers, the lowest accessible state in the electron cascade process is the  $2 p_0$  state. Effective mass theory predicts a binding energy of 11 meV for the  $2 p_0$  excited state of a single donor in silicon<sup>4)</sup>. If the charge state of the A-center in Si:Se was known, the binding energy of the ground state could then be deduced. Although we were unable to prove that the A- and B-centers are different charge states of a selenium related double donor<sup>6,7)</sup>, many of our results are not in contradiction with such an interpretation. Assuming a doubly charged center, the energy separation between the  $2 p_0$  state and the conduction band is expected to be about 44 meV. Adding this value to  $E_2$  gives a binding energy relative to the ground state of about 0.57 eV. This result is not unreasonable as seen from Fig. 6, where the arrow (F) indicates a value of 0.568 eV. It should be noted, however, that this interpretation is only valid if the lowest state in the electron cascade process is the  $2 p_0$  state, even though it is separated by about 20 meV from the state immediately above.

Although broadening effects may limit the resolution of the capacitance technique, the  $\sigma_{nA}^0$  spectrum of Si:Se nevertheless shows three clearly resolved peaks in the energy region between 0.53 eV and 0.56 eV. To demonstrate this, we replot the spectrum at 40 K in this energy region on an expanded scale in Fig. 9. To the best of our knowledge, no detailed information on the excited states of the selenium related donors in silicon is available and we can therefore only speculate on the origin of these peaks. Scaling the energies of excited states for shallow donors<sup>2,5)</sup> one might expect the energy spacing between the  $2 p_{\pm}$  and  $2 p_0$  excited states to be about 20 meV if we again assume that the A-center is doubly charged. Following our previous assignment of the  $2 p_0$  state, a peak in the spectrum at about 0.54 eV may then be anticipated, in agreement with

the data shown in Fig. 9 where the arrow over the first peak indicates an energy of 0.543 eV. Assuming that the peak at 0.543 eV is due to the  $2 p_{\pm}$  state, the energies of the  $3 p_{\pm}$  and  $4 p_{\pm}$  states can then readily be deduced by again scaling the energies of excited states for shallow donors. According to Ref. 2 and 5 the energy spacings between the  $2 p_{\pm}$  state and the  $3 p_0$  and  $4 p_{\pm}$  states are 4 meV and 17 meV, respectively, if the charge on the empty A-center is two. These energy spacings are indicated by the two additional arrows in Fig. 9. The predicted values agree surprisingly well with the other two peaks present in the measured spectrum, although obviously further investigations are needed before an unambiguous assignment of the spectrum is possible. Adding the scaled effective mass binding energy of the  $4 p_{\pm}$  state to the peak energy of the transition from the ground state into the  $4 p_{\pm}$  state we arrive at an ionization energy of 0.570 eV for the A-center. This is indicated by the arrow F in Fig. 9.

The other type of excited states involved in the spectra is states originating from the multivalley nature of the conduction band<sup>1)</sup>. These states may lie well below the conduction band and we believe that the low energy part of the spectrum below 0.53 eV is produced by such states. Expanding this region of the 110 K spectrum (Fig. 10), three peaks can be distinguished. Of these three peaks, the one at the lowest energy (labelled T) is clearly resolved whereas the other two (labelled M and N) are less easily observed. If only the peak at 0.426 eV is due to a transition from the ground state to an excited state, the spectrum can be understood in terms of a center having a  $T_d$  symmetry. Although the ground state in this case is split into a non-degenerated  $A_1$  ground state, a triply degenerated  $T_2$  state and a double degenerated E state (without taking spins into account),  $T_d$

symmetry only allows a dipole transition from the  $A_1$  ground state to the  $T_2$  excited state. The other two peaks must then be due to other effects. One possibility is that they are phonon replicas of the main peak<sup>31)</sup>. If all three peaks are involved in transitions from the ground state to excited states, the A-center must have a lower symmetry. A possible lower symmetry which might account for the presence of three peaks is  $C_{3V}$ . Such a symmetry arises, for example, when defects form pairs.

The line shape of the peak at 0.426 eV further confirms the interpretation that the peak is caused by a bound-to-bound transition. In order to show this, we have fitted the experimental data with a Lorentzian line shape whose halfwidth is 8 meV. It has already been mentioned that the energy position of the peak is constant in the temperature range studied. This implies that the energy position of the ground state may also be independent of temperature if it is assumed that the state causing this peak is effective mass like. On the other hand this could mean that the wave function of the ground state gets its main contribution from the bottom of the conduction band and that any influence of the valence band is weak. Such a conclusion is supported by the observation that the capture cross section  $\sigma_{nA}^t$  of electrons probably exceeds the capture cross section  $\sigma_{pA}^t$  of holes by several orders of magnitude and that the photoionization cross section  $\sigma_{nA}^0$  of electrons is much larger than the photoionization cross section  $\sigma_{pA}^0$  of holes (Fig. 2).

If the ground state of the A-center is pinned to the conduction band, one would expect that the energy spacing between the ground state and the valence band decreases with increasing temperature in the same way



as the forbidden energy gap <sup>32)</sup>. In Fig. 11, we replot the 40 K and 160 K data of Fig. 8. The corresponding decrease of the bandgap in this temperature range is 13 meV <sup>33)</sup>. Although the shift of the threshold energy is clearly comparable with this value, we did not perform any further analysis due to the lack of well-established theoretical models for  $\sigma_p^0$  and the weak temperature broadening of the spectra which additionally complicates any attempt of interpretation. No accurate value of the threshold energy  $E_A$  can therefore be given. However, extrapolating the data of Figs. 8, 11 and 12, it is readily seen that a value of about 0.59 eV is obtained for  $E_A$  at 40 K. Adding  $E_A$  to the binding energy of the ground state (about 0.57 eV), a value of 1.16 eV is obtained which is very close to the value of the band-gap of silicon at 40 K (1.1695 eV).

It should be mentioned that from the temperature dependence of the thermal emission rate  $e_{pA}^t$  an enthalpy  $\Delta H = 0.57$  eV is obtained <sup>6)</sup>, if it is assumed that the capture cross section of holes,  $\sigma_{pA}^t$ , is independent of temperature. Furthermore, we believe that the weak structure of the 40 K spectrum at about 0.65 eV is probably caused by spin-orbit splitting of the valence band <sup>30)</sup> (Fig. 11). It is interesting to note that a linear plot of  $\sigma_{pA}^0$  (Fig. 12) in the energy interval between 0.67 eV and 0.77 eV yields a straight line. We have no explanation for this behavior.

The corresponding data for the sulfur-related A-center in silicon are in many respects very similar with those for Si:Se, although there are several remarkable differences. Unlike the  $\sigma_{nA}^0$  spectrum in Si:Se, the low energy part of the  $\sigma_{nA}^0$  spectrum for the sulfur-related A-center increases more slowly at 40 K. This is shown in Fig. 13, where the 40 K data for  $\sigma_{nA}^0$  have been replotted on an expanded scale. As a consequence of the broader spectrum, more than three peaks are observed in the



energy region between 0.53 eV and 0.59 eV. However, comparing the data in Fig. 13 with those of Fig. 9, the close resemblance of the spectra is quite evident. The three peaks of the  $\sigma_{nA}^0$  spectrum in Si:S marked with arrows have exactly the same energy spacing and relative position in the spectrum as the three peaks in Si:Se. Although this results does not necessarily justify any further interpretation of the spectrum, it is nevertheless tempting to try the same assignment as for Si:Se (Fig. 13). Assuming again that the A-center is doubly charged and keeping in mind Krag and Zeigers data <sup>11)</sup>, that the  $2 p_0$  state of sulfur in silicon is 20.6 meV below the  $2 p_{\pm}$  state, one expects the  $2 p_0$  state to have an energy position at about 0.546 eV. It is readily seen from Fig. 13 that this value is close to the threshold energy of the  $\sigma_{nA}^0$  spectrum in agreement with what is expected according to our earlier arguments. If it is further assumed that the A-center in Si:S is effective mass like, the lower edge of the conduction band should then lie about 44 meV above the  $2 p_0$  state at 0.59 eV (Fig. 13, arrow F) in agreement with previous investigations <sup>8)</sup>.

These results are in good agreement with the optical spectra but are difficult to understand with respect to previous data obtained from investigations of the thermal emission rate <sup>7)</sup>. These studies gave a "thermal activation energy" of 0.587 eV which is expected to be the value of  $E_2$ , i.e., of the energy spacing between the ground state and the lowest accessible state in the electron capture cascade process. If this value is taken as the spacing between the ground state and the  $2 p_0$  excited state, as we did in the case of Si:Se, the binding energy of the A-center would be about 0.631 eV. This seems to be far too large compared with the spectrum presented in Figs. 5 and 13 and the threshold energy of  $\sigma_{pA}^0$  (Fig. 7). On the other hand, the value of

0.587 eV for  $E_2$  is very close to the spacing of the  $4 p_{\pm}$  state from the ground state as obtained from the tentative assignment shown in Fig. 13.

In a recent optical study of isotopic effects in Si:S<sup>22)</sup>, Forman reported several absorption lines with peaks at 0.561 eV, 0.569 eV, 0.573 eV, and 0.588 eV. Although the author has a different assignment of the lines (claiming that the strongest three lines all represent  $1 s - 2 p_{\pm}$  transitions of slightly different centers), these values are in excellent agreement with the spectrum shown in Fig. 13.

At temperatures above 120 K, the Si:S samples became optically sensitive for energies below 0.52 eV (Fig. 5). As in the case of Si:Se, there is reason to believe that this part of the  $\sigma_{nA}^0$  spectrum originates from the multivalley nature of the conduction band<sup>2)</sup>. Replotting the low energy part of the 160 K spectrum of  $\sigma_{nA}^0$  on an expanded scale (Fig. 14), it is readily seen that the data for the sulfur related A-center differ somewhat from those obtained in Si:Se (Fig. 10). Although measurements in the energy region between 0.44 eV and 0.48 eV were not disturbed by interfering absorption bands in air and the data obtained were fairly reproducible, no smooth spectrum in Si:S could be obtained in this energy region. Furthermore, the low energy tail of the spectrum is considerably broader than for Si:Se with an unmistakable (Fig. 5) tendency for a structure to develop. It is interesting to observe that a value of 0.370 eV obtained from Hall effect and absorption measurements is often quoted in the literature for the energy position of a sulfur related center<sup>12)</sup> in silicon. As can be seen from the data shown in Fig. 14, this is very close to the threshold energy of the  $\sigma_{nA}^0$  spectrum at temperatures above 120 K. On the other hand, the main peak of the spectrum (Fig. 14) has a halfwidth of 14 meV and a peak energy of

0.427 eV which are almost exactly the same values as observed for the corresponding peak in Si:Se. This is remarkable because, from a comparison of the data shown in Figs. 9 and 13, it is evident that the A-center in Si:S is about 25 meV deeper than in Si:Se. This result clearly shows that the resemblance between sulfur and selenium in silicon is not at all so close as is sometimes assumed. As mentioned earlier, the energy position of the peak at 0.427 eV is independent of temperature at all temperatures investigated. For an effective mass like state, this implies that the ground state of the A-center is also independent of temperature. Bearing in mind the fact that the capture cross sections  $\sigma_{nA}^t$  and the photoionization cross sections  $\sigma_{nA}^o$  of electrons are much larger than the capture cross sections  $\sigma_{pA}^t$  <sup>7)</sup> and photoionization cross sections  $\sigma_{pA}^o$  of holes in Si:S (Fig. 1) and using the same arguments as for Si:Se, it might again be concluded that the wavefunction of the ground state is mainly built up by contributions from the conduction band.

If the ground state of the A-center in Si:S is pinned to the conduction band, the energy spacing between the center and the top of the valence band should decrease with increasing temperature. This is indeed observed as shown in Fig. 7. We have replotted the spectrum of  $\sigma_{pA}^o$  for 40 K and 160 K (Fig. 15) in order to show that the two spectra coincide for energies larger than about 0.7 eV and that a possible temperature shift of the threshold energy cannot therefore be obtained by simply shifting one of the curves along the energy axes. Closer inspection of Fig. 15 shows that there is a small temperature broadening of the spectra at lower energies which makes any analysis of the data even more difficult. However, it is readily seen qualitatively that the temperature shift of the threshold energy is of the order of 15 meV

which should be compared with the decrease of the bandgap (13 meV) in this temperature range. We therefore feel that these results are not in contradiction with a possible pinning of the A-center to the conduction band. It has already been pointed out that a linear plot of  $\sigma_{PA}^0$  in Si:Se gives a straight line in a limited energy interval. This behaviour is still more pronounced in Si:S (Fig. 16), where the linear region extends from about 0.61 eV to 0.81 eV at 160 K.

As in the case of Si:Se, no comparison was made between measured  $\sigma_{PA}^0$  data and calculated photoionization cross sections. An attempt can be made to determine the spacing between the A-center and the top of the valence band  $E_A$  in Si:S at 40 K by extrapolating the corresponding  $\sigma_{PA}^0$  spectra in Figs. 15 and 16. In both cases, a value of about 0.57 eV is obtained. If the value of 0.59 eV for the binding energy of the A-center at 40 K derived above is added to  $E_A$ , a value of 1.16 eV is obtained which is in good agreement with the bandgap of silicon at 40 K. This suggests that while the optical data in Si:S are reasonably well understood the thermal data for the A-center<sup>7)</sup> still need further interpretation, which is in contrast to the situation in Si:Se, where data of both kinds are satisfactory accounted for.

#### IV b. The shallower donor levels (B-centers)

Next, we want to discuss the selenium related B-center in silicon. Closer inspection of Fig. 4 shows that the low energy part of the spectral distribution is dominated by a peak surprisingly sharp for a spectrum obtained with junction space charge techniques. We have replotted this part of the  $\sigma_{nB}^0$  spectrum on an enlarged scale in Fig. 17, where we also compare the experimental data with a Lorentzian line shape with a halfwidth of 1.7 meV. Although the halfwidth may decrease with improved resolution the good agreement between the measured and calculated line shapes, suggests that the peak at 0.270 eV originates

from transitions between the ground state of the selenium related B-center and a state generated by the multivalley nature of the conduction band. Further analysis of these data along the lines of that for the A-center is at present not possible since the measurements are disturbed by the presence of water absorption bands in the region between 0.275 eV and 0.290 eV.

In spite of these disturbances, the measurements were accurate enough to reveal some structure at the edge of the  $\sigma_{nB}^0$  spectrum above 0.28 eV. The resolution was, however, not good enough to permit a detailed analysis. We tend to believe that this structure can be understood in terms of excited states due to a Rydberg series. Assuming that the B-center is effective mass like, the deepest of these excited states should then be the  $2 p_0$  state. If the excited states are broadened due to, e.g., the electric field in the junction, it is anticipated that the photoionization cross section will increase rapidly for energies larger than  $E_2$ , the energy separation between the ground state and the  $2 p_0$  state, instead of showing a series of well-defined sharp peaks. Comparing the absorption data of Forman<sup>22)</sup> with the results presented in Fig. 13, it can be anticipated that some kind of broadening effects seems to occur in junction measurements. Previous thermal measurements<sup>6)</sup> gave a value of 0.286 eV for  $E_2$  which is in good agreement with the threshold energy of the spectrum shown in Fig. 4. This further supports the assignment that in the case of the B-center the value of  $E_2$  is indeed the spacing between the ground state and the  $2 p_0$  state<sup>6)</sup>. Hence, using this result and knowing the spacing between the bottom of the conduction band and the  $2 p_0$  state, we are able to calculate the binding energy of the selenium related B-center in silicon.

From detailed measurements of capture cross sections and using the arguments of Gibb et al.<sup>29)</sup>, a value of 14 meV for the spacing between the conduction band and the  $2 p_0$  state was previously obtained. For a single donor in silicon, effective mass theory predicts 11 meV which is in good agreement with observed values for shallow donors (e.g., 11 meV for Si:P)<sup>2)</sup>. Neutral selenium (and sulfur) contain two electrons in the bound state and, when one of them is excited, the resulting spectrum is more complicated. If the band minimum were spherical, the spectrum would be analogous to that of the one-electron excitation spectrum of the helium atom. Because of anisotropy, the spectrum is modified. No detailed calculations have been attempted, but it can easily be deduced<sup>34)</sup> that, except for additional small multiplet splittings, the spectrum is the same as that of a single shallow donor. The  $2 p_0$  equivalent state is, however, expected to have a larger binding energy than in the case of a single donor, because selenium and sulfur have two extra protons in the nucleus, one of which is only partially screened by the electron remaining in the ground state<sup>34)</sup>. Thus, the value of 14 meV obtained from our analysis is reasonable. Adding 14 meV to  $E_2$  gives a value of 0.301 eV for the binding energy of the selenium related B-center in silicon. This is indicated by an arrow (F) in Fig. 4.

It should be noted that the energy spacing between the peak at 0.270 eV and the optical ionization energy of 0.301 eV is 31 meV. This result is in good agreement with corresponding observations of shallow centers in silicon<sup>2)</sup> and very close to the value quoted by Ning and Sah<sup>9)</sup> for transition between the ground state and the  $T_2$  excited state in Si:S. Furthermore, the energy position of the peak at 0.270 eV is independent

of temperature which may indicate that the B-center is pinned to the conduction band in agreement with previous thermal data <sup>6)</sup>.

The overall features of the  $\sigma_{nB}^0$  spectra for the sulfur related B-center in silicon are very similar to those of Si:Se. The spectral distribution of  $\sigma_{nB}^0$  has previously been measured by Ning and Sah <sup>9)</sup>. They found a peak at 0.285 eV which they explained as transitions from the  $1sA_1$  ground state to the  $1sT_2$  excited state. Replotting the data of Fig. 3 in this energy region on an expanded scale shows that we observe a peak at 0.286 eV which fits well to a Lorentzian line shape with a halfwidth of 2.5 meV (Fig. 18).

The spectral distribution of  $\sigma_{nB}^0$  at about 0.290 eV has not been further analysed because of disturbance from water absorption bands in the air. However, we are convinced that the structure observed above 0.30 eV is not due to experimental difficulties but is caused by Coulombic excited states. Using the same arguments as for the B-center in Si:Se, an increase of  $\sigma_{nB}^0$  is expected for energies larger than  $E_2$ , the energy spacing between the ground state and the  $2p_0$  state. From the temperature dependence of the thermal emission rate analysed in terms of a model suggested by Gibb et al., <sup>29)</sup> a value of 0.302 eV has previously been obtained for  $E_2$  of the B-center in Si:S <sup>7)</sup>. Comparing this result with the spectrum shown in Fig. 3, it is quite evident that there is a sharp increase in  $\sigma_{nB}^0$  at exactly this energy, thus confirming our previous interpretation of  $E_2$ . From measurements <sup>7)</sup> of the capture cross section  $\sigma_{nB}^t$  we had to conclude that the energy spacing between the bottom of the conduction band and the  $2p_0$  state is about 17 meV. Adding this energy value to  $E_2$  gives a value of 0.319 eV for the binding energy of the sulfur related B-center in silicon, which is close to the value quoted by Ning and Sah <sup>9)</sup> and in good agreement with the optical data (see arrow F in Fig. 3).



The energy separation between the peak at 0.286 eV and the conduction band is then 33 meV in accordance with a singly charged center derived from previous theoretical considerations<sup>18)</sup>.

There appears to be no temperature dependence of the position of the peak at 0.286 eV, indicating that also the position of the ground state is temperature independent if the B-center is effective mass like. It is then expected that the enthalpy  $\Delta H_{nB}$  of the center is equal to the optical ionization energy  $\Delta G_{nB}^0$ . From previous thermal measurements<sup>7)</sup>, a value of 0.320 eV has been obtained for  $\Delta H_{nB}$  whereas the Gibbs free energy<sup>35)</sup>  $\Delta G_{nB} = \Delta G_{nB}^0 - kT \ln g$  was temperature dependent and smaller than  $\Delta H_{nB}$ . If it is concluded from the optical data that the B-center is pinned to the conduction band, a degeneracy factor  $g$  close to 2 is obtained by putting  $\Delta H_{nB} = \Delta G_{nB}^0$ . This value of  $g$  gives a temperature dependence of  $\Delta G_{nB}$  which is in fair agreement with previous experimental results<sup>7)</sup>.

It is interesting to note that the peak at 0.286 eV due to intravalley optical transitions is about 16 meV "deeper" than the corresponding peak in Si:Se, in agreement with the 19 meV larger binding energy of the B-center in Si:S. However, the dominating peaks of the A-centers due to intravalley optical transitions have almost identical energy positions in Si:Se and Si:S, although the A-center in Si:S has a 25 meV larger binding energy.

## V. Conclusion

Two dominant donor levels have been observed in both selenium and sulfur doped silicon. One of these centers (the A-center) is a midgap level whereas the other one (the B-center) has a binding energy of 0.301 eV



in Si:Se and 0.320 eV in Si:S. The spectra of the photoionization cross section of electrons,  $\sigma_n^0$ , have been analysed by assuming that the B-centers are singly charged and the A-centers doubly charged. With this assumption, good agreement between our results of the A-centers and published data of shallow donors in silicon has been obtained for the Rydberg excited states.

Similar good agreement has been obtained for the valley orbit split off states of the B-centers and those for shallow centers in silicon. The  $T_2$  state has been found to lie 33 meV and 31 meV below the conduction band in Si:S and Si:Se, respectively. The corresponding values for the A-centers are 163 meV and 143 meV, respectively.

Within this model we have strong reasons to believe that the energy position of the B-centers with respect to the conduction band is independent of temperature. Similar temperature independent energy positions have been observed for the A-centers at  $E_c - 0.590$  eV in Si:S and at  $E_c - 0.57$  eV in Si:Se. The spectra of the photoionization cross section of holes,  $\sigma_{pA}^0$ , are not in contradiction with a possible pinning of the A-centers to the conduction band.

#### Acknowledgements

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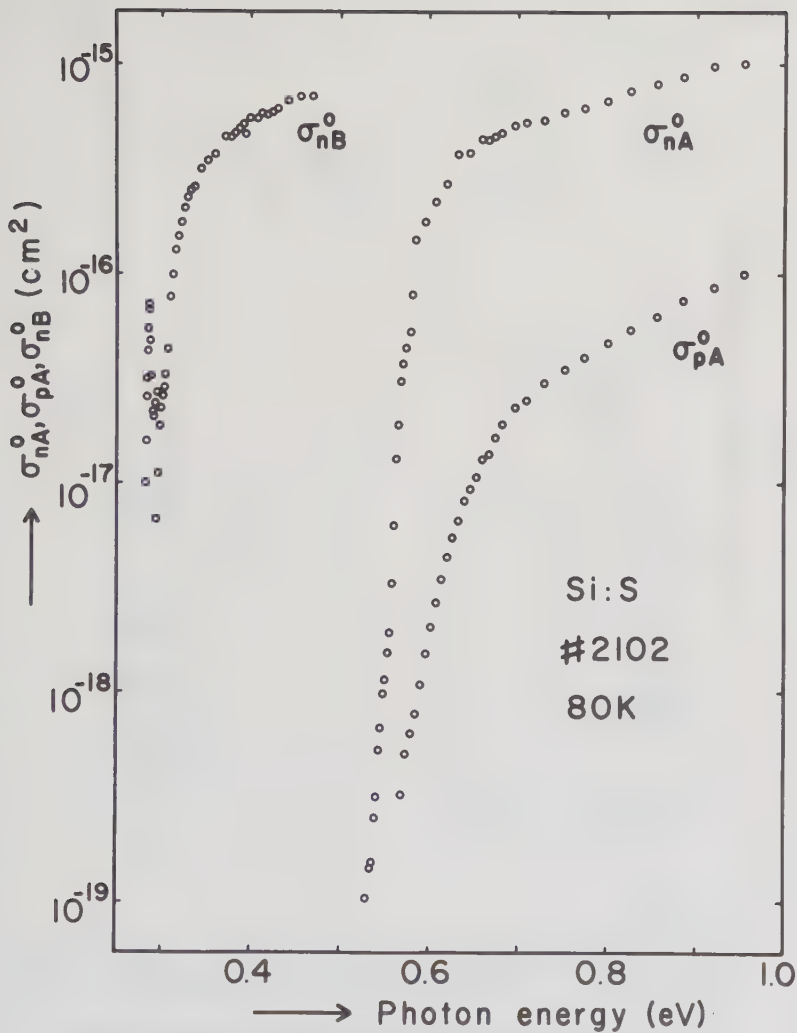


Fig.1. A survey of the absolute values of the photoionization cross sections  $\sigma_{nA}^0$ ,  $\sigma_{pA}^0$  and  $\sigma_{nB}^0$  versus photon energy in sulfur doped silicon.

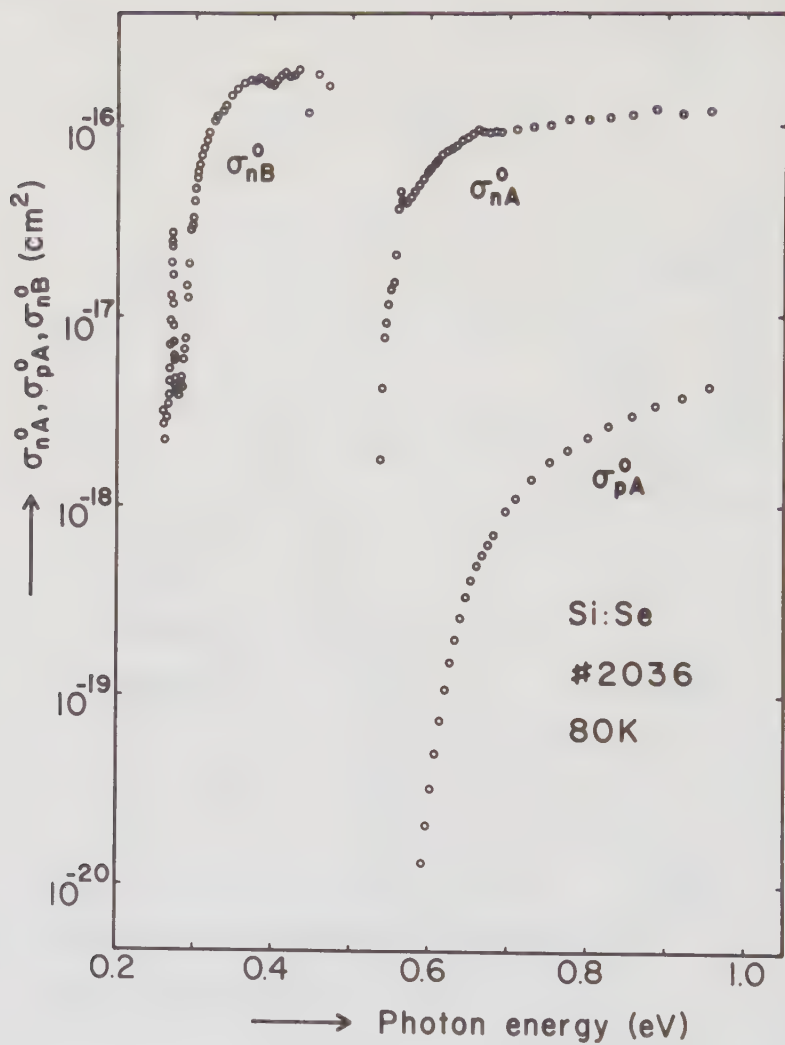


Fig.2. A survey of the absolute values of the photoionization cross sections  $\sigma_{nA}^0$ ,  $\sigma_{pA}^0$  and  $\sigma_{nB}^0$  versus photon energy in selenium doped silicon.

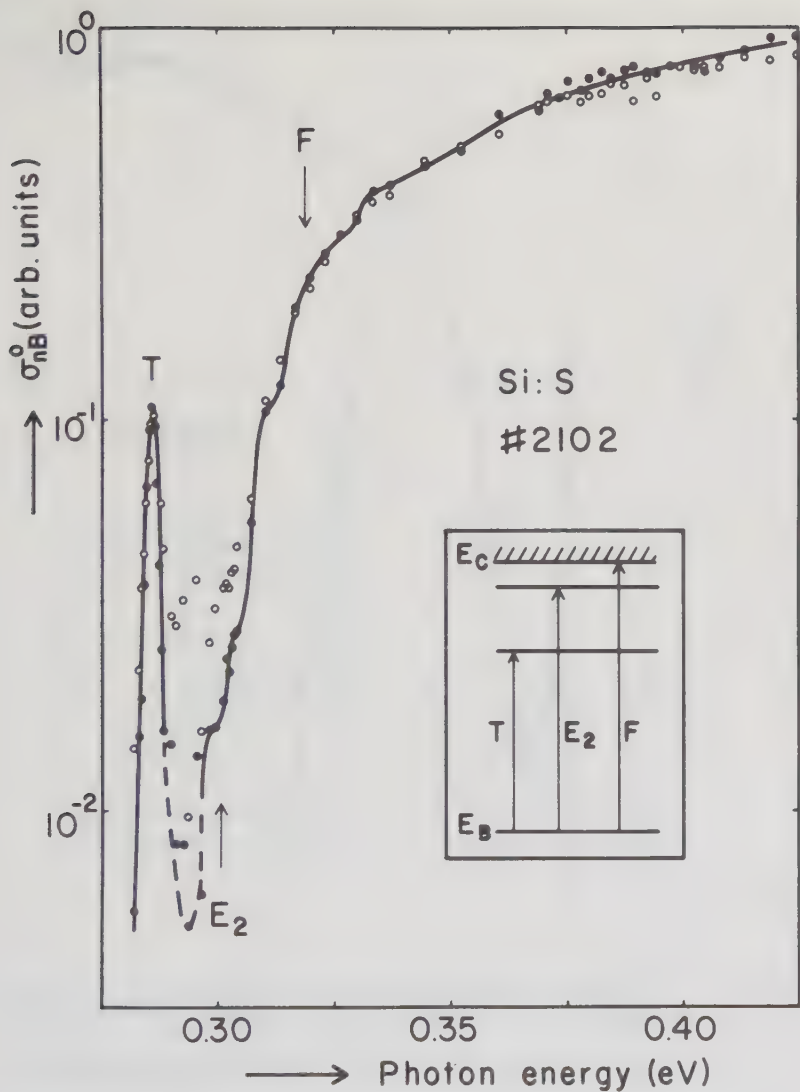


Fig.3. Spectra of the photoionization cross section of electrons,  $\sigma_{nB}^0$ , for the shallower donor level in Si:S at two different temperatures ( $\bullet$  = 40K;  $\circ$  = 80K).

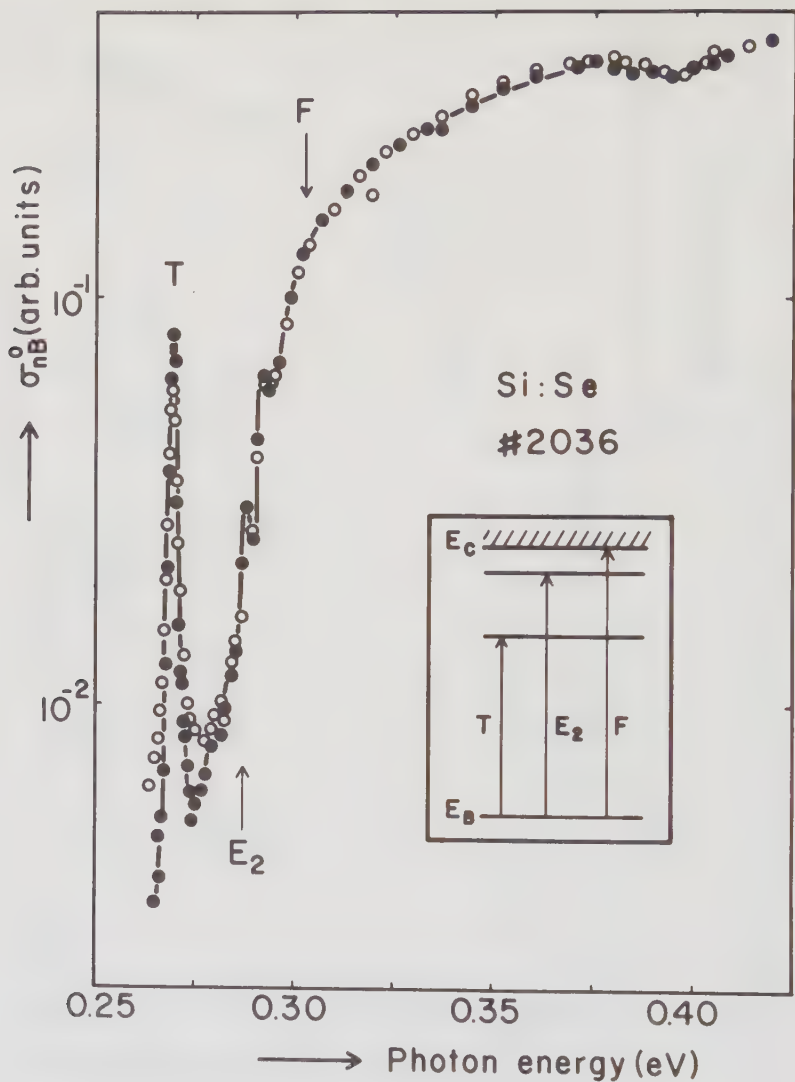


Fig.4. Spectra of the photoionization cross section of electrons,  $\sigma_{nB}^0$ , for the shallower donor level in Si:Se at two different temperatures ( $\bullet$  = 40K;  $\circ$  = 80K).

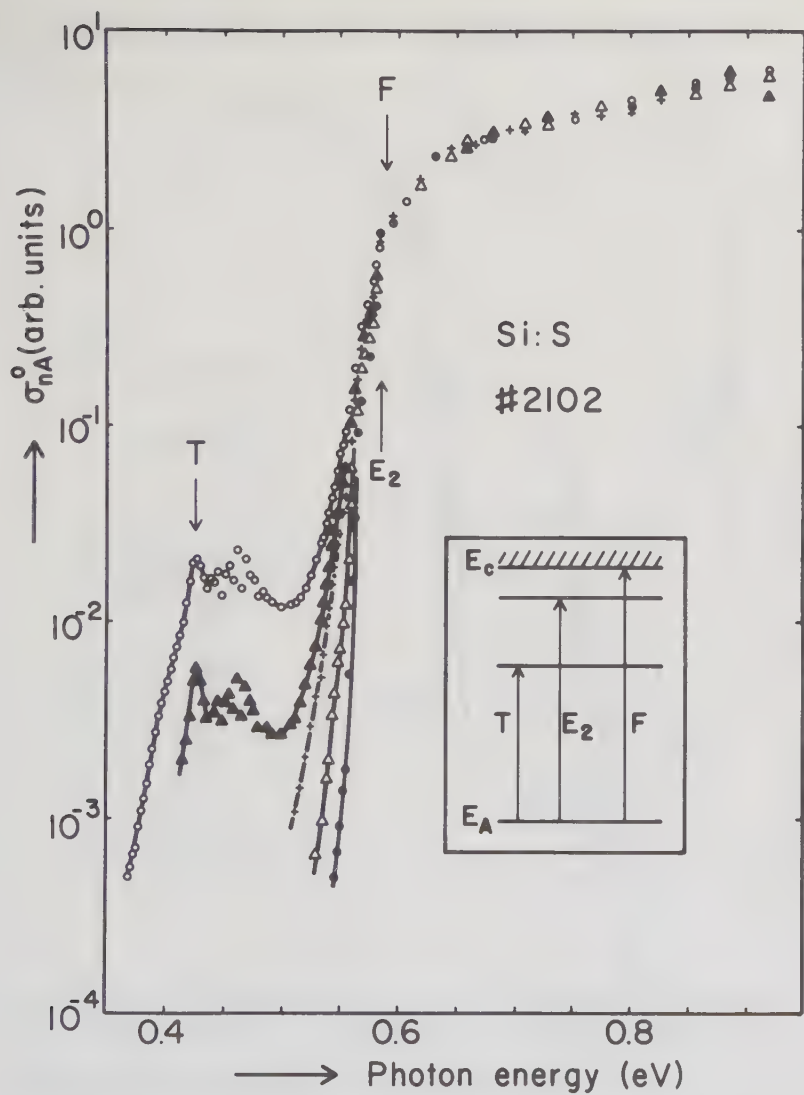


Fig.5. Spectra of the photoionization cross section of electrons,  $\sigma_{nA}^0$ , for the deeper donor level in Si:S at different temperatures ( $\bullet$  = 40K,  $\Delta$  = 80K, + = 120K,  $\blacktriangle$  = 140K,  $\circ$  = 160K).



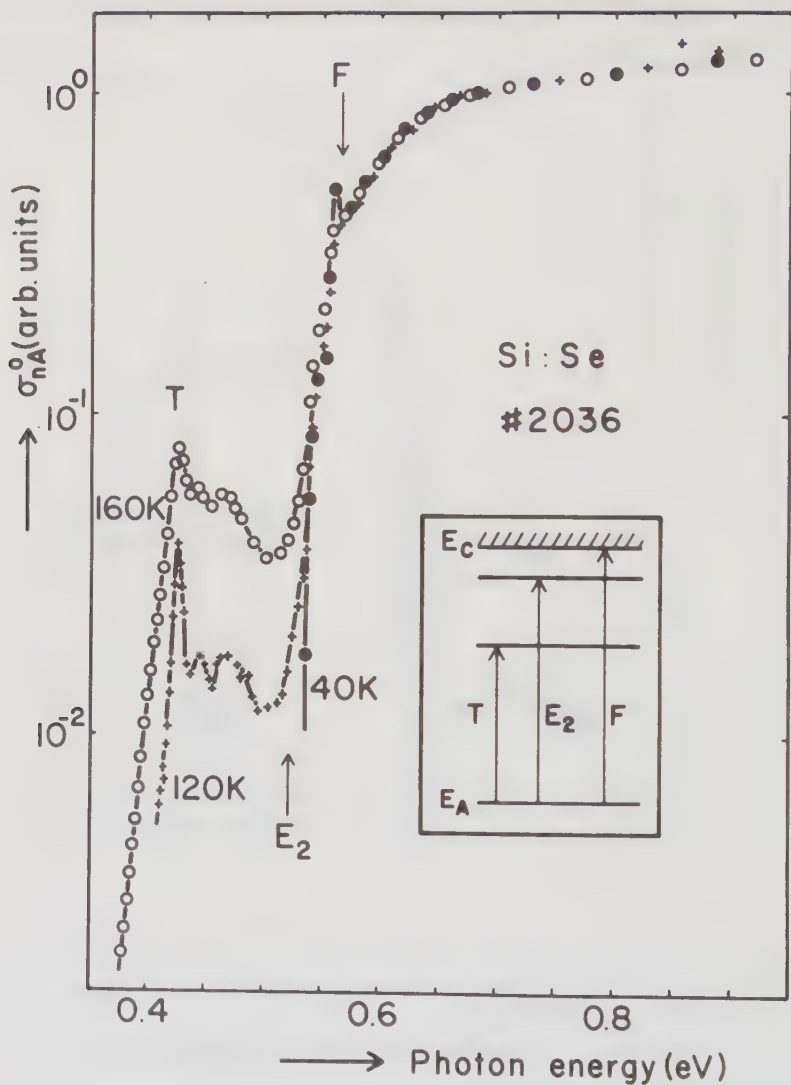


Fig.6. Spectra of the photoionization cross section of electrons,  $\sigma_{nA}^0$ , for the deeper donor level in Si:Se at different temperatures ( $\bullet$  = 40K, + = 120K,  $\circ$  = 160K).

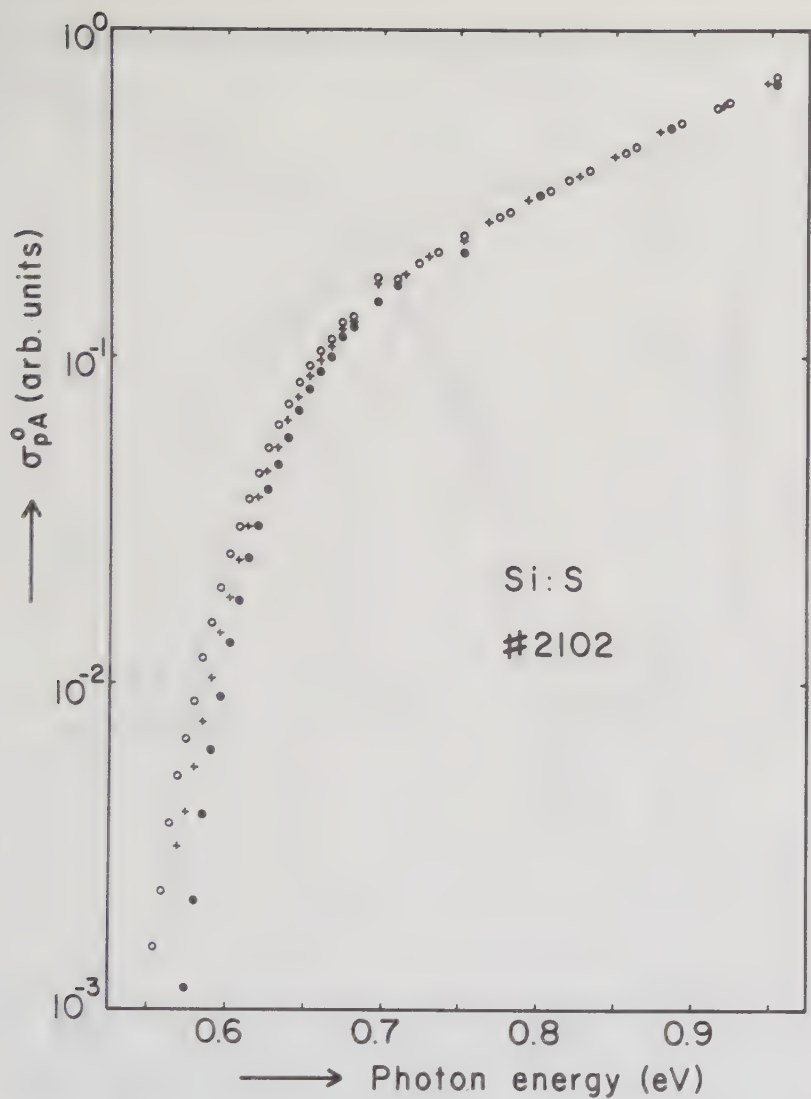


Fig.7. Spectra of the photoionization cross section of holes,  $\sigma_{pA}^0$ , for the deeper donor level in Si:S at different temperatures ( $\bullet$  = 40K, + = 120K,  $\circ$  = 160K).

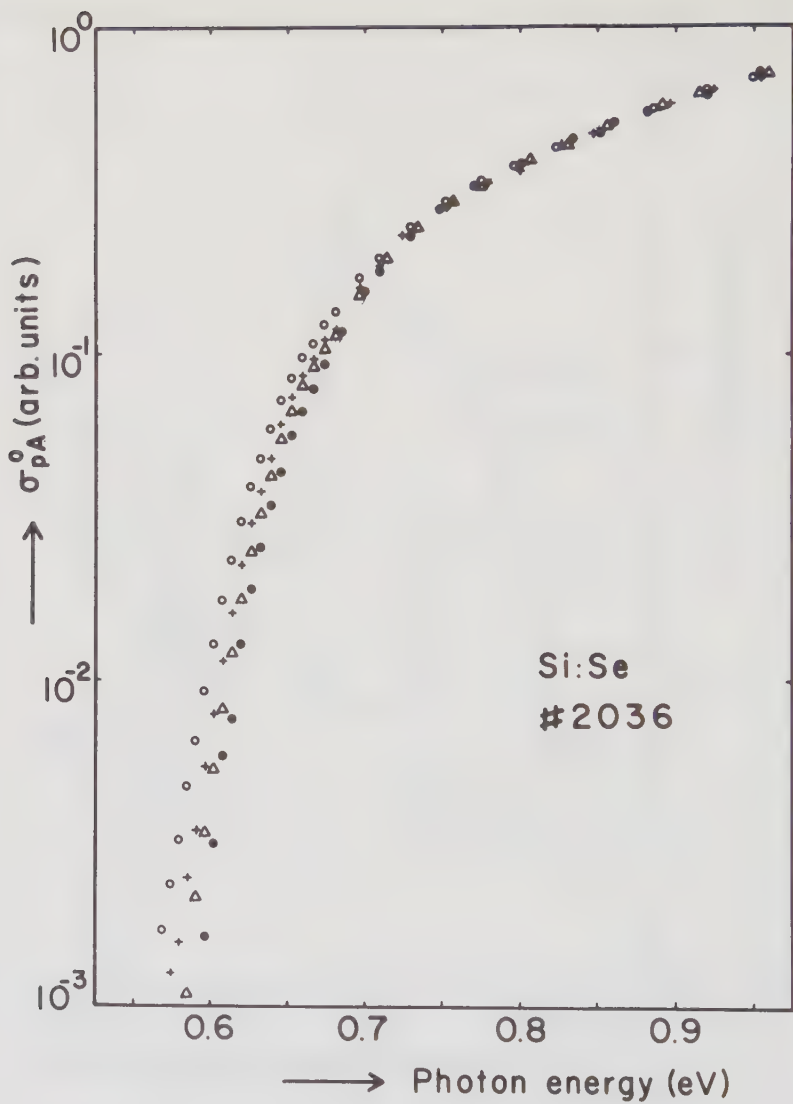


Fig.8. Spectra of the photoionization cross section of holes,  $\sigma_{pA}^0$ , for the deeper donor level in Si:Se at different temperatures ( $\bullet$  = 40K,  $\circ$  = 80K,  $+$  = 120K,  $\Delta$  = 160K).

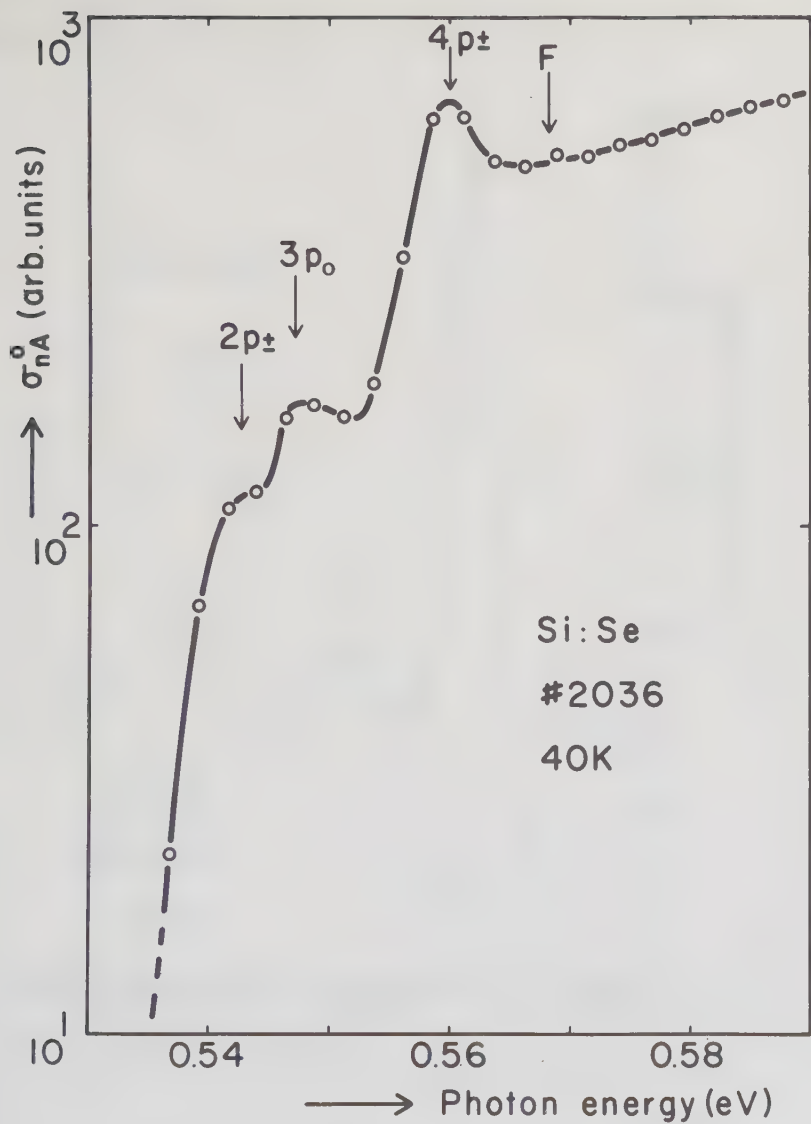


Fig.9. An enlarged part of the continuum region for  $\sigma_{nA}^0$  in Si:Se showing the influence and assignment of the excited states.

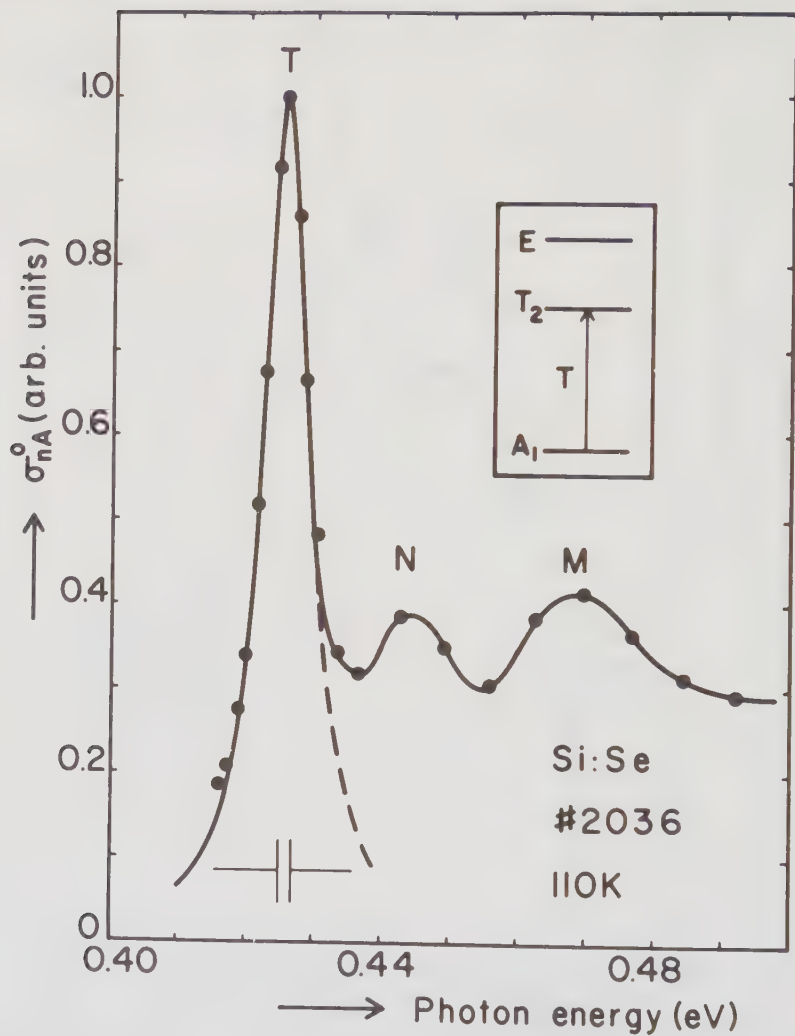


Fig.10. High resolution spectra of the low energy region for  $\sigma_{nA}^0$  in Si:Se showing the Lorentzian behavior of the main peak and some additional structure (see text).

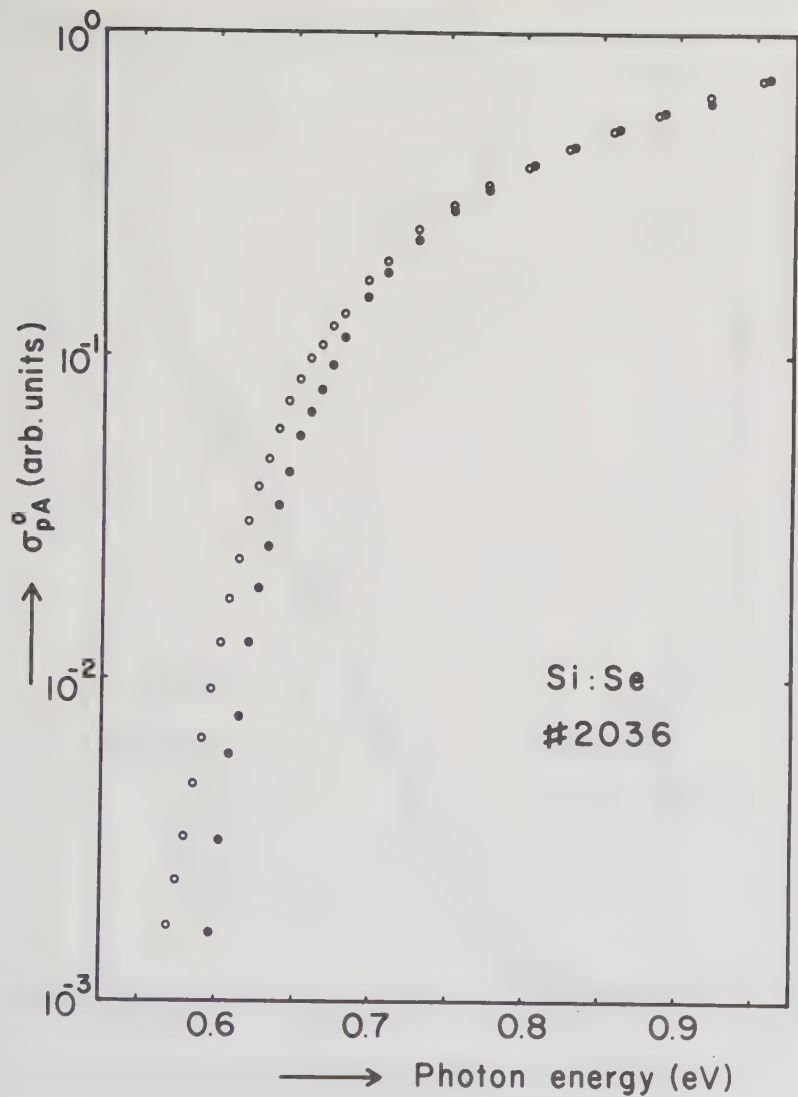


Fig.11. Comparison of  $\sigma_{pA}^0$  at 40K (●) and 160K (○) showing the energy shift and temperature broadening of the edge region with increased temperature.

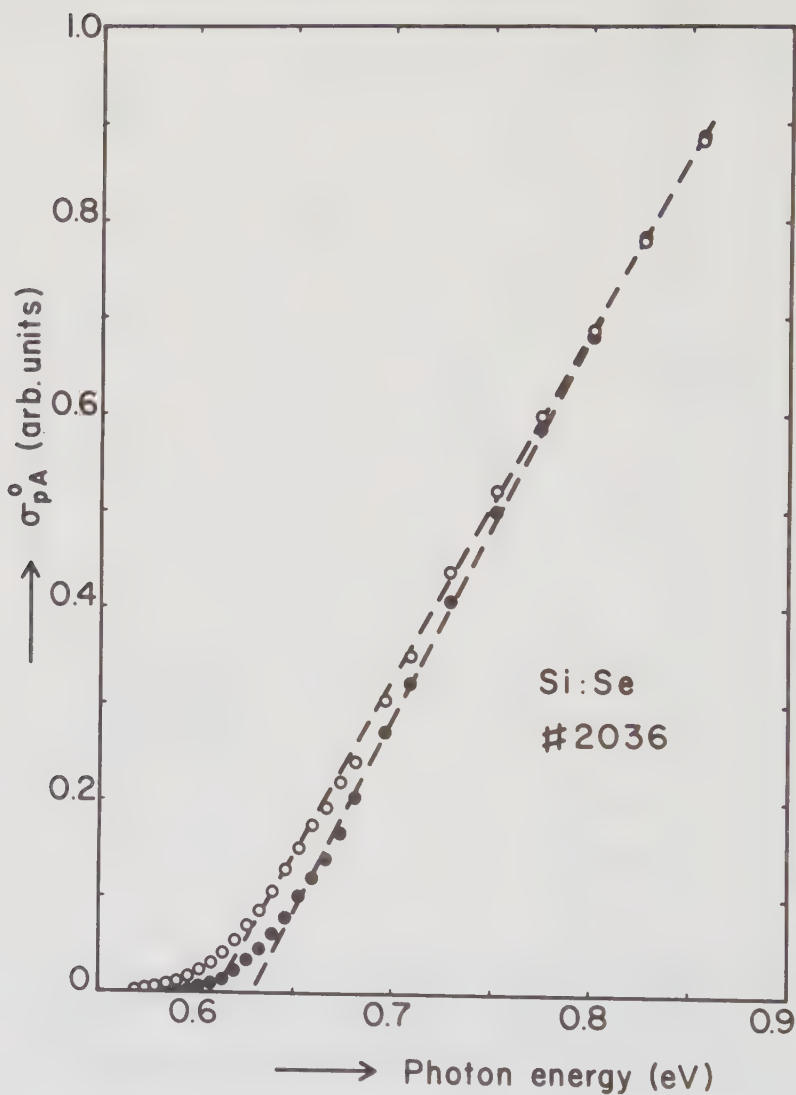


Fig.12. Linear plot of  $\sigma_{pA}^0$  at 40K (●) and 160K (○) showing the linear behavior of  $\sigma_{pA}^0$  with photon energy.

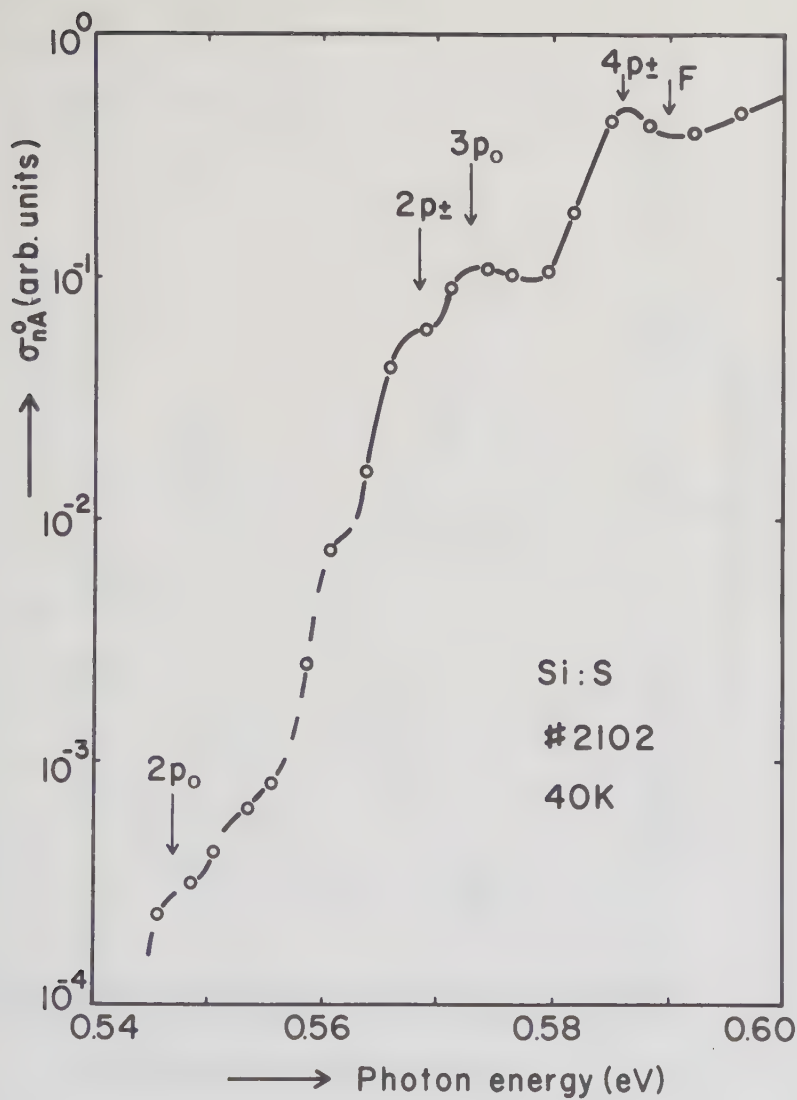


Fig.13. An enlarged part of the continuum region for  $\sigma_{nA}^0$  in Si:S showing the influence and the assignment of the excited states.



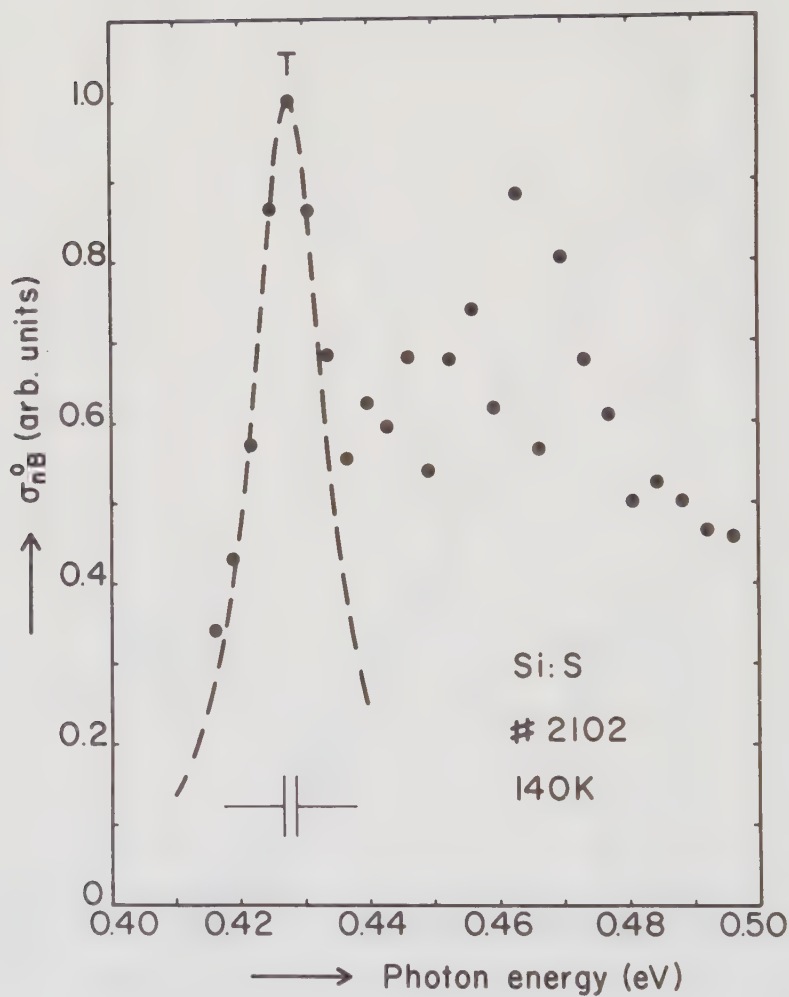


Fig.14. High resolution spectrum of the low energy region for  $\sigma_{nA}^0$  in Si:S showing the Lorentzian behavior of the main peak and some additional structure (see text).

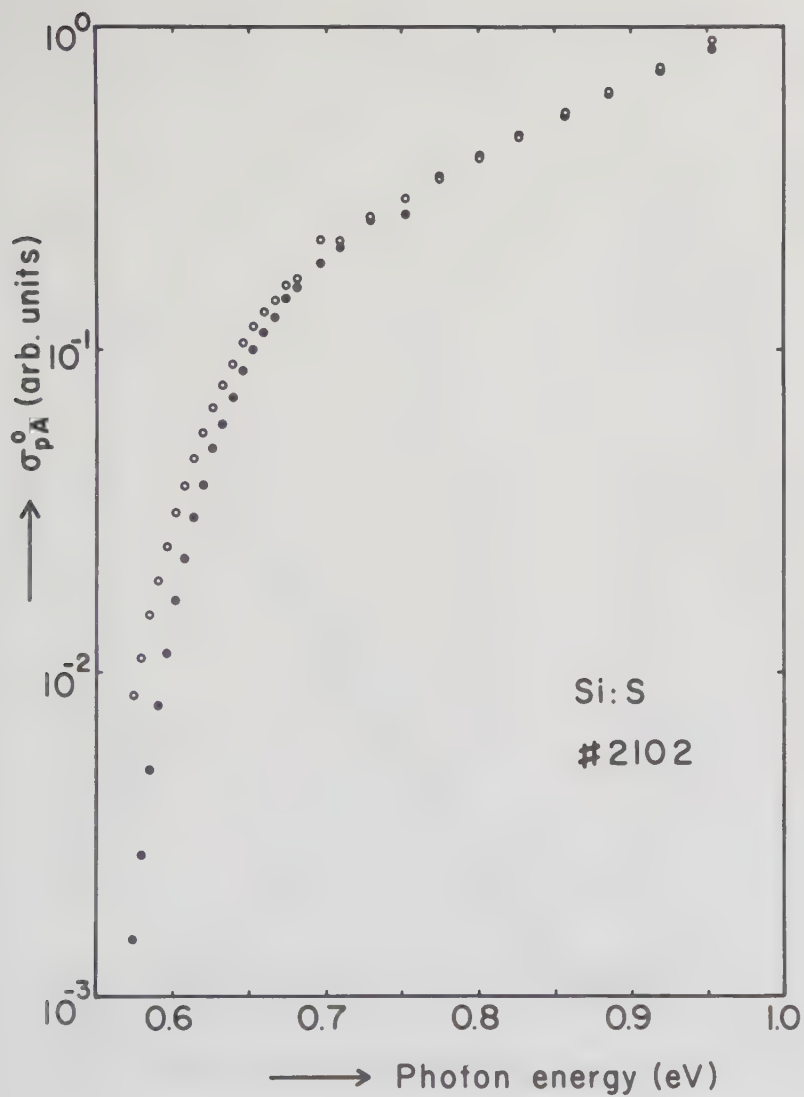


Fig.15. Comparison of  $\sigma_{pA}^0$  at 40K (●) and 160K (○) showing the energy shift and temperature broadening of the edge region with increased temperature.

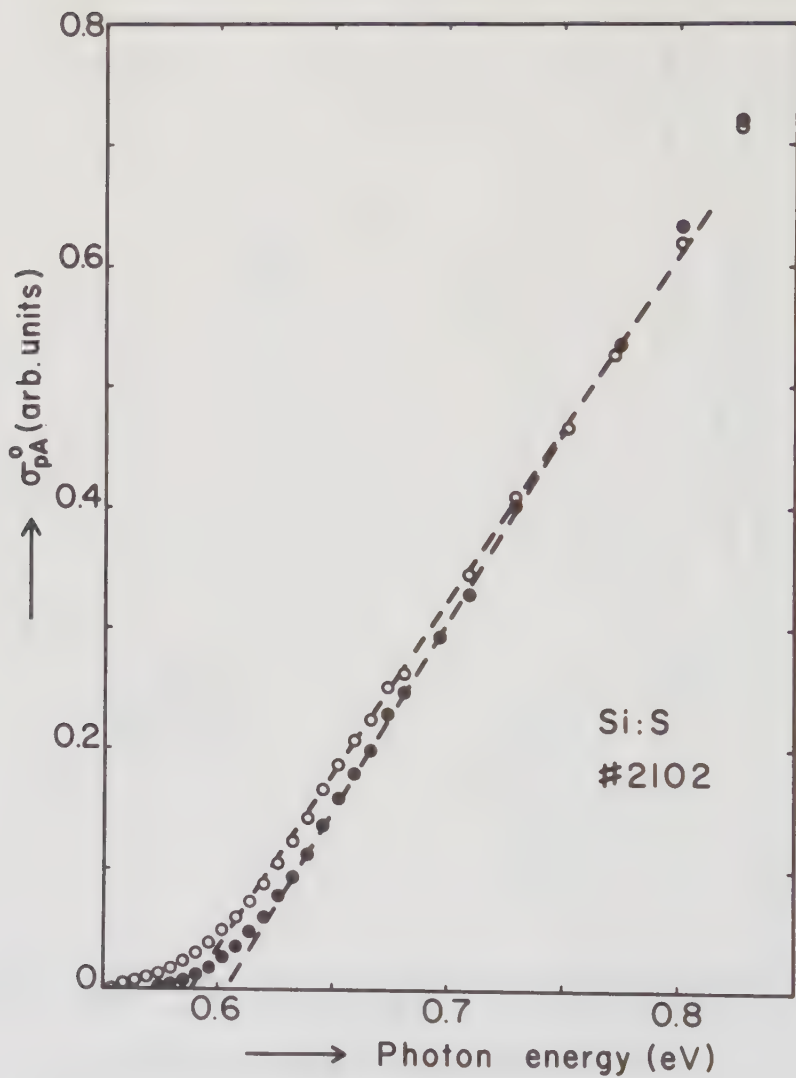


Fig.16. Linear plot of  $\sigma_{pA}^0$  at 40K (●) and 160K (○) showing the linear behavior of  $\sigma_{pA}^0$  with photon energy.

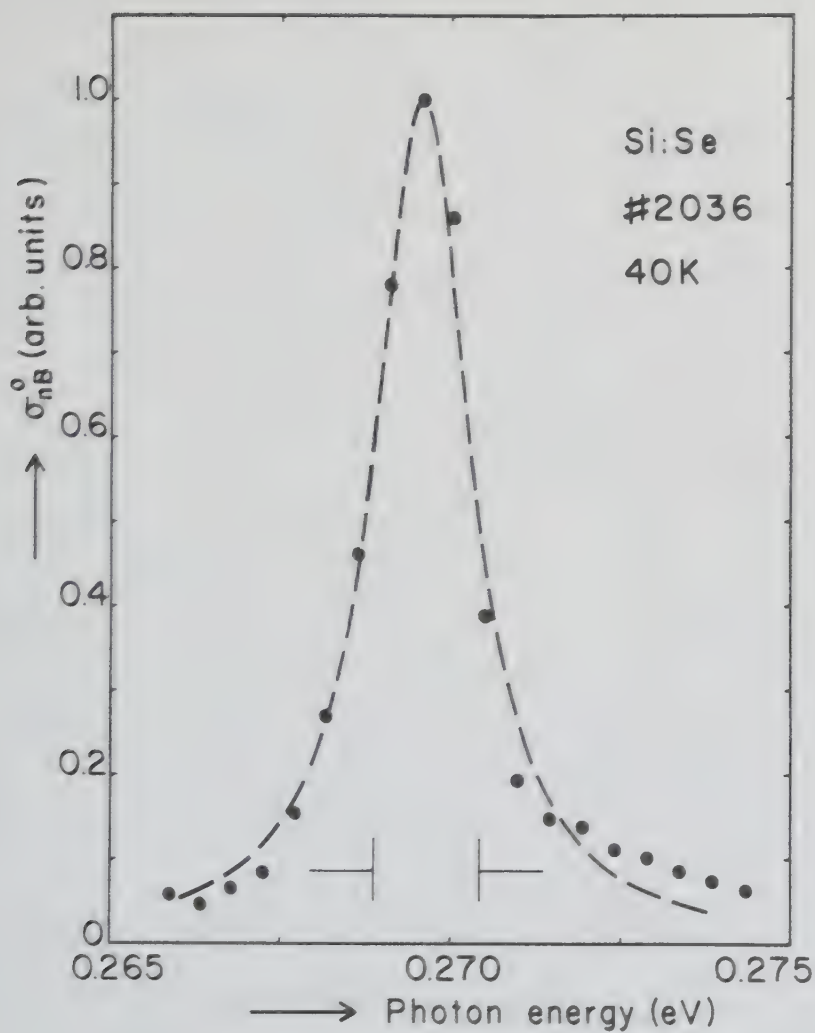


Fig.17. An enlarged part of a high resolution spectrum in the low energy region of  $\sigma_{nB}^0$  in Si:Se showing the Lorentzian behavior of the main peak.

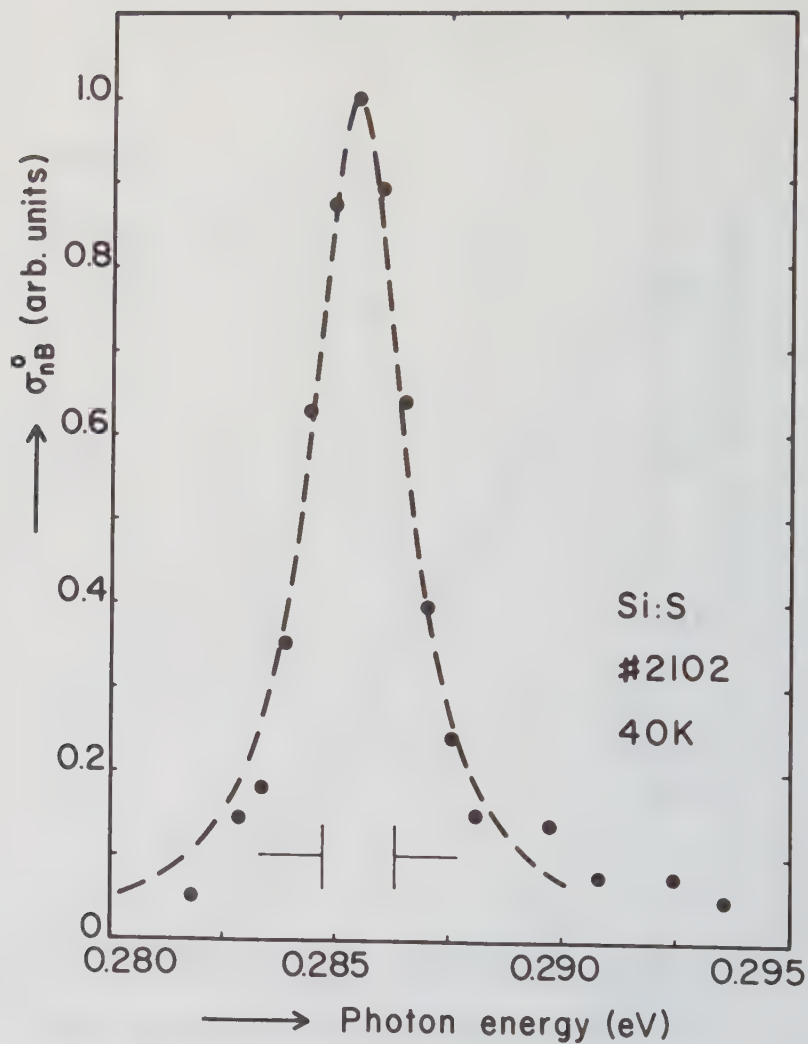


Fig.18. An enlarged part of a high resolution spectrum in the low energy region of  $\sigma_{nB}^0$  in Si:S showing the Lorentzian behavior of the main peak.





## Chemical identification of deep energy levels in Si:Se

by

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### Abstract

Profiles of deep energy states in selenium diffused silicon  $p^+n$  junctions have been studied by junction capacitance techniques and Secondary Ion Mass Spectrometry (SIMS). In both cases similar profiles are obtained. Since the profiles measured by SIMS are due to selenium atoms, it is concluded that selenium is responsible for the two dominant energy levels previously investigated in Si:Se by junction space charge techniques.



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### I. Introduction

One of the major problems encountered in the study of defects in semiconductors is the chemical identification of the defect investigated. Under favourable circumstances, different kinds of spin resonance techniques may reveal not only the atom causing the defect but also its local environment. Very often, however, these techniques are not sensitive enough for the study of deep energy levels or are even not applicable due to the lack of spin effects. In this paper a different approach which makes it possible to relate unambiguously an energy level investigated by electrical measuring techniques with a particular foreign atom is advanced.

Chemical species are often introduced into silicon by diffusion. For convenience, diffusion is usually allowed to proceed for such a long time that part of the semiconductor being studied gets a homogeneous distribution of the foreign atoms. In some cases the impurity-host system is such as to permit control of the diffusion in a well-

defined manner by changing diffusion time and temperature. It is then possible to place the diffusion profile in the space charge region of a pn-junction where it can be studied by well-known junction space charge techniques<sup>1,2)</sup>. One of the systems suitable for this kind of investigation is selenium in silicon.

Detailed measurements of the electrical and optical properties of Si:Se published recently<sup>3,4)</sup> show that selenium diffusion gives rise to two dominant donor levels at  $E_c - 0.30$  eV and  $E_c - 0.57$  eV, respectively<sup>4)</sup>. In this paper, we would like to present results on the diffusion profiles of these centers. The profiles have been measured with three different methods. Two of these methods are Deep Level Transient Spectroscopy (DLTS)<sup>5)</sup> and Constant Capacitance Spectroscopy (CCS). These enable one to measure concentration profiles of deep centers electrically without, however, yielding information on the chemical nature of the centers. The third method used is Secondary Ion Mass Spectrometry (SIMS)<sup>6,7,8,9)</sup> which measures the concentration profile of a particular chemical species, in our case selenium. It will be shown that the results obtained with these three methods are in good agreement and that the two energy levels created by selenium diffusion have similar diffusion profiles. Finally, the data presented in this paper will be compared with previously published data on selenium diffusion in silicon.

## II. Experimental details

The  $p^+n$  diodes used in our investigations were selenium diffused at temperatures between 900 °C and 1100 °C for periods from 10 minutes to 3 1/4 hours. The geometry of the samples and the diffusion procedures have previously been described in Ref. 3.

Since  $p^+n$  junctions were used, the diffusion profiles measured by junction techniques could only be investigated in the n-region of the diode. Hence, the width of the  $p^+$  region had to be determined separately using an electron scanning microscope in the Electron Beam Induced Current (EBIC)<sup>6)</sup> mode. In this mode, a cleaved surface perpendicular to the junction area in which the space charge region is exposed is bombarded with electrons creating electron-hole pairs. If this creation takes place within a carrier diffusion length  $L$  from the space charge region, a current will flow in an external circuit. Usually  $L$  is of the order of 100  $\mu\text{m}$  in the bulk material and hence much larger than the width of the neutral n- and p-regions of the diode. At the surface, however, the effective diffusion length is decreased due to surface states which act as very efficient recombination centers. In our investigations, we bombarded with 5 keV electrons for a period of a few minutes which resulted in an effective diffusion length for holes of a few microns.

On the EBIC picture shown in Fig. 1, the region with the highest induced current is displayed as a white area. The profile of the induced current is also shown. Knowing the width of the space charge region from capacitance measurements and assuming that the maximum contribution of the induced current originates from the middle of the space charge region, a value of 1.8  $\mu\text{m}$  for the width of the  $p^+$  region is obtained from the EBIC picture.

DLTS-profiling has been performed as follows. At a quiescent reverse bias  $V_R$  resulting in a diode capacitance  $C$ , voltage pulses of height  $V_1$  are applied to the diode thus decreasing the reverse bias to  $V_R - V_1$  (Fig. 2a). During the pulses, the width of the space charge region

decreases from  $W$  to  $W_1$ . This implies that the deep energy levels are filled with electrons not only in the region  $(W - \lambda) - W_1$ , but also in the region  $\lambda^*$  due to the exponential tail of the free carriers in the neutral  $n$  region (Fig. 2b). It should be noted that  $\lambda^*$  is independent of the applied voltage but dependent on the pulse length<sup>10</sup>. In Fig. 2,  $\Delta C(V_1)$  is the initial magnitude of the capacitance transient following pulses of height  $V_1$ . Otherwise conventional notations are used.

Changing the pulse height from  $V_1$  to  $V_1 + \delta V_1 = V_2$  the average concentration of deep energy levels  $\bar{N}_T$  in the region between  $W_1(V_R - V_2) - \lambda^*$  and  $W_1(V_R - V_1) - \lambda^*$  can be obtained from the following relation

$$\bar{N}_T (W_1 - \lambda^*) = \frac{\overline{W_1}}{W_1 - \lambda^*} \cdot \frac{q \epsilon \epsilon_0 A^2 N_d^2}{C^3} \cdot \frac{\Delta C(V_2) - \Delta C(V_1)}{\delta V_1} \quad (1)$$

Details of how eqn 1 is obtained are given in the appendix where also a method for the determination of  $\lambda^*$  is described. Apart from the factor  $W_1/(W_1 - \lambda^*)$ , eqn 1 is identical with that given in Ref. 5. The extra factor arises from the fact that the region where the deep centers are filled with electrons during the pulse is larger than that where the shallow energy levels are completely neutralized by the injected free electrons.

DLTS profiling is difficult to perform when the concentrations of shallow and deep energy levels are about the same<sup>11</sup>). We therefore used the CCS technique in these cases. The measuring procedures were as follows:

The sample was first cooled to 77 K with forward bias in order to make sure that all deep energy levels were filled with electrons. The diode was then reverse biased by applying an external voltage  $V_{Ri}$ . Under these circumstances, the total potential drop over the junction can be written as

$$V_i = \frac{q}{\epsilon \epsilon_0} \int_0^W x N_d(x) dx = V_D + V_{Ri} \quad (2)$$

where  $V_D$  is the diffusion voltage. The diode was then heated up ionizing the deep centers. Since the capacitance was kept constant, the reverse bias increased. When all deep energy levels were ionized, the diode was again cooled to 77 K still keeping the capacitance constant. The potential drop is now given by

$$V_f = \frac{q}{\epsilon \epsilon_0} \left\{ \int_0^W x N_d(x) dx + \int_0^{W-\lambda'} x N_T(x) dx \right\} = V_D + V_{Rf} \quad (3)$$

and hence the change of the potential due to the ionization of the deep center can be written as

$$\Delta V = V_f - V_i = V_{Rf} - V_{Ri} = \frac{q}{\epsilon \epsilon_0} \int_0^{W-\lambda'} x N_T(x) dx. \quad (4)$$

Although  $\lambda'$  is defined in general terms, it can nevertheless be measured under certain circumstances.

The measuring procedure is repeated for different capacitance values and  $\Delta V$  measured as a function of  $W$ . Differentiating eqn. 4, the following relation is obtained:

$$\frac{\partial}{\partial W} \Delta V(W) = \frac{q}{\epsilon \epsilon_0} (W - \lambda') N_T \quad (x = W - \lambda') \quad (5)$$

If  $N_T$  is constant for small values of  $W$ , a straight line is obtained when  $\frac{\partial}{\partial W} \Delta V(W)$  is plotted versus  $W$ .  $N_T$  is then calculated from the slope and the intersection with the abscissa gives  $\lambda'$ . If, for larger values of  $W$ ,  $N_T$  starts to decrease, a plot of  $\frac{\partial}{\partial W} \Delta V(W)/(W - \lambda')$  versus the distance from the surface given by  $W - \lambda' + x_0$ , where  $x_0$  is the width of the  $p^+$  region gives the concentration profile.

In the case of Si:Se, each measurement consisted of two temperature cycles at the same capacitance value in order to analyse the two donor levels independently. The level at  $E_c - 0.30$  eV has been studied by cooling the sample to 77 K at a constant capacitance value. The diode has then been heated up to a temperature at which all the 0.30 eV levels were empty but all the 0.57 eV levels still filled with electrons. After cooling the sample again down to 77 K, a voltage change,  $\Delta V_1$ , has been obtained (Fig. 3) which is proportional to the concentration of 0.30 eV levels in this particular region of the junction. The sample has then been heated up until all 0.57 eV levels were empty still keeping the initial capacitance value constant. After cooling the diode down to 77 K again, the reverse bias had further increased by a value of  $\Delta V_2$ . In this manner, the diffusion profiles of the two donor levels could be investigated independently of each other.

SIMS<sup>6,8,9)</sup> is a completely different method than the two methods described above. Here a small portion of the sample surface is bombarded with primary ions, in our case  $Ar^+$  ions. The secondary ions sputtered off the surface are analyzed in a mass spectrometer. By peeling off successive layers of atoms, the sputtering beam eats its way toward the interior of the sample, usually at a constant rate. By

plotting the  $^{80}\text{Se}$  ion current versus time, which is proportional to depth, the diffusion profile is obtained. The  $^{80}\text{Se}$  isotope was found most suitable for quantitative recording of the secondary ion current since the other Se isotope peaks in the mass spectrum were significantly contaminated with aggregates such as  $\text{SiO}_3^-$  and  $\text{Si}_2\text{CN}$ .

It should be noted that SIMS measures the total concentration of  $^{80}\text{Se}$  atoms in the sample (in our case down to ppb) whereas the capacitance techniques measure the concentration of electrically active deep centers relative to the concentration of shallow centers. The concentration of shallow centers is usually six or seven orders of magnitude smaller than that of the host atoms. In principle one can therefore say that the capacitance techniques have higher sensitivities allowing the absolute magnitude of the concentration to be determined with greater accuracy than using SIMS<sup>12)</sup>. However, due to the correction factors originating from the  $\lambda$ -region, SIMS is preferable when an accurate value of the diffusion coefficient is needed, provided the concentration is high enough for its use to be feasible.

### III. Results and discussion

Measurements have been performed on diodes diffused at four different temperatures, 900 °C, 960 °C, 1000 °C and 1050 °C. In order to increase the accuracy of our investigation, we used three different diffusion times at 960 °C. In the analysis, the surface of the semiconductor is assumed to attain the solubility concentration  $C_0$  of selenium in silicon immediately. The selenium concentration  $C$  inside the sample then follows the relation<sup>13)</sup>

$$C(x) = C_0 \operatorname{erfc} (x/2 \sqrt{Dt}) \quad (6)$$

where  $x$  is the distance from the surface,  $D$  the diffusion coefficient at the diffusion temperature used and  $t$  the diffusion time. It is readily seen from Fig. 4 that the data obtained are obviously well described by eqn. 6. Furthermore, it is interesting to note that the diffusion mechanisms are evidently the same in the  $p^+$  region heavily doped with boron and in the phosphorous doped  $n$ -region.

The results are summarized in Table I in which a comparison with previous investigations is also made. In these investigations, different kinds of surface conductivity and Hall effect measurements combined with either angle lapping or layer removal<sup>14-16)</sup> were used. Table I clearly shows that there is good agreement between our data and previous results. It is also evident that different diffusion times at a constant temperature give about the same diffusion coefficient.

Fig. 5 shows results which have been obtained from SIMS, CCS and DLTS measurements in a sample diffused at 900 °C for 3 1/4 hours. In order to fit the capacitance data, the SIMS data have been shifted down by a factor of 6. If only a fraction of the Se atoms are electrically active, the (chemical) concentration measured by SIMS should be larger than the (electrical) concentration obtained by the capacitance techniques. However, no further analysis of this point has been performed since the SIMS concentration calibration may be wrong by an order of magnitude<sup>12)</sup>. It is quite evident from Fig. 5 that the three methods give similar results. We also present separate diffusion profiles for the 0.30 eV and 0.57 eV levels (Fig. 5). Since the agreement between the two sets of data is good we conclude that similar diffusion mechanisms are involved for both the 0.30 eV and the 0.57 eV levels in Si:Se.



There is no doubt that the diffusion profiles measured by SIMS are due to selenium. Since SIMS and capacitance measurements give the same diffusion profiles, we are confident that the defect centers which have been studied in Refs. 3 and 4 are selenium related centers involving selenium either substitutionally, interstitially, or as a ligand in a more complicated structure.

#### IV. Acknowledgements

We gratefully acknowledge the assistance of Karl Nideborn in performing the EBIC measurements and valuable discussions with Lars-Ake Ledebö. The authors would also like to thank the Swedish Natural Science Research Council and the Swedish Board for Technical Development for financial support.

#### Appendix: Capacitance profiling

From Poisson's equation and assuming that the shallow donor concentration  $N_d$  is constant, the following relations can be deduced<sup>17)</sup>:

$$C = \frac{\epsilon \epsilon_0 A}{W}$$

$$V = \frac{q N_d W^2}{2 \epsilon \epsilon_0} + \int_0^{W-\lambda^*} \frac{x q N_T(x)}{\epsilon \epsilon_0} dx.$$

$\lambda^*$  has a value between zero and the thermal equilibrium value  $\lambda = \sqrt{\frac{2 \epsilon \epsilon_0 (E_F - E_T)}{q^2 N_d}}$  depending on the experimental conditions.  $C$  is the high frequency capacitance and  $V$  is the sum of the applied reverse bias  $V_R$  and the diffusion voltage. It is further assumed that  $N_T \ll N_d$  which means that, to a good approximation,  $W$  is given by

$$W = \sqrt{\frac{2 \epsilon \epsilon_0 V}{q N_d}}.$$

During the measurements, the bias is reduced from  $V_R$  to  $V_R - V_1$  for a short while and then returned to its quiescent value (Fig. 2a). After the pulse has been applied, the deep levels are filled in the region between  $W(V_1) - \lambda^* = W_1 - \lambda^*$  and  $W(V_R) - \lambda$  (Fig. 2b). Since the reverse bias is unchanged, the depletion width has changed by an amount  $\Delta W$ , which is monitored as a small change in the capacitance  $\Delta C$ . From eqn A 1 one gets

$$N_d W \Delta W = \int_{W_1 - \lambda^*}^{W - \lambda} x N_T(x) dx. \quad (A 3)$$

Since  $\frac{\Delta W}{W} = -\frac{\Delta C}{C}$ , it follows that

$$\Delta C = -\frac{C}{W^2 N_d} \int_{W_1 - \lambda^*}^{W - \lambda} x N_T(x) dx \quad (A 4)$$

During the profiling experiment,  $V_1$  is changed and, hence,  $W_1$  and  $\Delta C$  are altered. Differentiating eqn A 4 and rearranging the factors, the following result is obtained:

$$N_T(W_1 - \lambda^*) = \frac{W_1}{W_1 - \lambda^*} \cdot \frac{q \epsilon \epsilon_0 A^2 N_d^2}{C^3} \left| \frac{\delta(\Delta C)}{\delta V_1} \right| \quad (A 5)$$

which is similar to eqn 1 if the change in pulse height is infinitesimal.

Information about  $\lambda^*$  can be obtained from a homogeneously doped sample, at large reverse bias. Putting  $V_1 = \Delta V$ , for small pulse heights, we obtain

$$W_1 = \sqrt{\frac{2 \epsilon \epsilon_0}{q N_d} (V - \Delta V)} \approx W - \frac{W}{2} \frac{\Delta V}{V} \quad (A 6)$$

From eqn A 4 follows that

$$\begin{aligned}
 -\Delta C &= \frac{C}{W^2 N_d} \frac{N_T}{2} \left[ (W-\lambda)^2 - (W_1-\lambda^*)^2 \right] \approx \\
 \frac{W-\lambda^*}{W} &= \frac{C}{W^2} \frac{\epsilon \epsilon_0 N_T}{q N_d} \Delta V - C \frac{N_T}{N_d} \frac{W-(\lambda+\lambda^*)/2}{W} \frac{\lambda-\lambda^*}{W}
 \end{aligned} \quad (A 7)$$

Hence, plotting  $-\Delta C$  versus  $\Delta V$  a straight line will be obtained. Its intersection with the ordinate  $-\Delta C(0)$  is given by

$$-\Delta C(0) = -C \frac{N_T}{N_d} \frac{W-(\lambda+\lambda^*)/2}{W} \frac{\lambda-\lambda^*}{W} \quad (A 8)$$

Combining eqns. 8 and 5, we obtain

$$\frac{\lambda-\lambda^*}{W} = \frac{\Delta C(0)}{\frac{\delta(\Delta C)}{\delta V_1}} \cdot \frac{1}{2V} \frac{1}{1 - \frac{\lambda+\lambda^*}{2(W-\lambda^*)}} \approx \frac{\Delta C(0)}{\frac{\delta(\Delta C)}{\delta V_1}} \cdot \frac{1}{2V} \quad (A 9)$$

For the 0.57 eV level,  $\lambda^*$  has been found to be  $0.73 \mu\text{m}$  which should be compared with a value of  $8 \mu\text{m}$  for  $W$  ( $V_R = 30 \text{ V}$ ). This implies that within one profiling experiment, the factor  $W_1/(W_1-\lambda^*)$  in eqn. A 5 changes from 1.1 to 1.8. Although, depending on the type of measurements, this change can often be neglected, it may nevertheless be of importance in the determination of diffusion coefficients.

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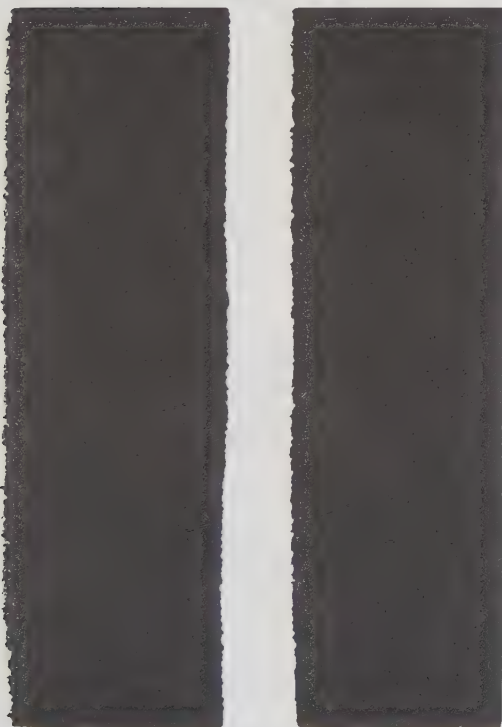
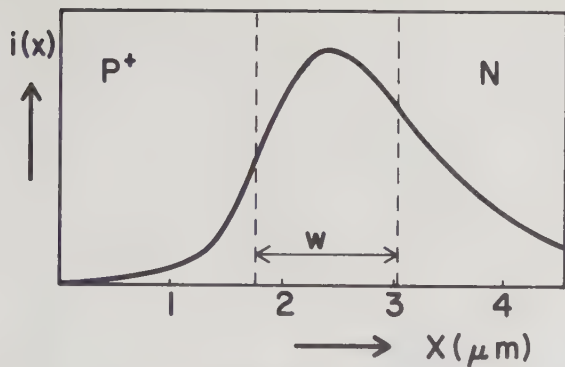
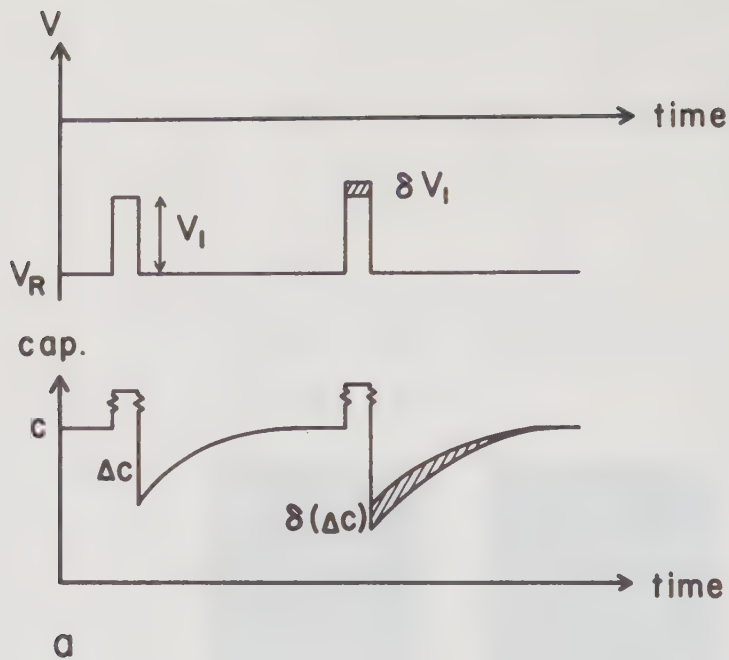
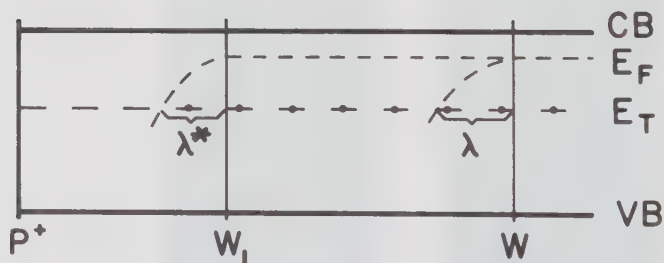


Fig.1. EBIC-picture of one of the  $p^+n$  diodes used in our diffusion experiments (c.f. Fig. 2 in Ref. 3). The white region corresponds to the middle of the junction. The profile of the induced current is shown above. (Due to the spatial distribution of excitation the current profile is smeared out).



a



b

Fig.2. Capacitance profiling: a) Pulse sequence and the corresponding capacitance transients. b) Energy band diagram of a  $p^+n$  diode illustrating the different "spill-over lengths" of electrons:  $\lambda^*$  during the pulse and  $\lambda$  at the quiescent reverse bias.

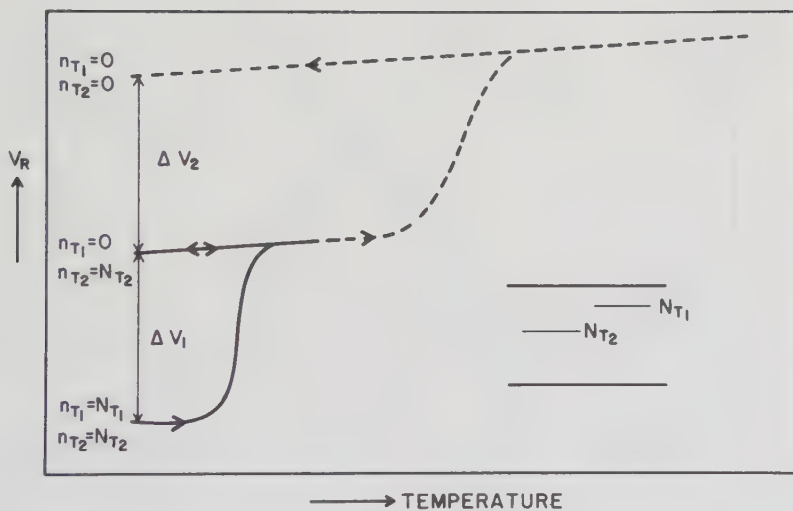


Fig.3. A constant capacitance profiling experiment in Si:Se.  $n_T$  is the electron occupancy of the deep centers. For details, see text.



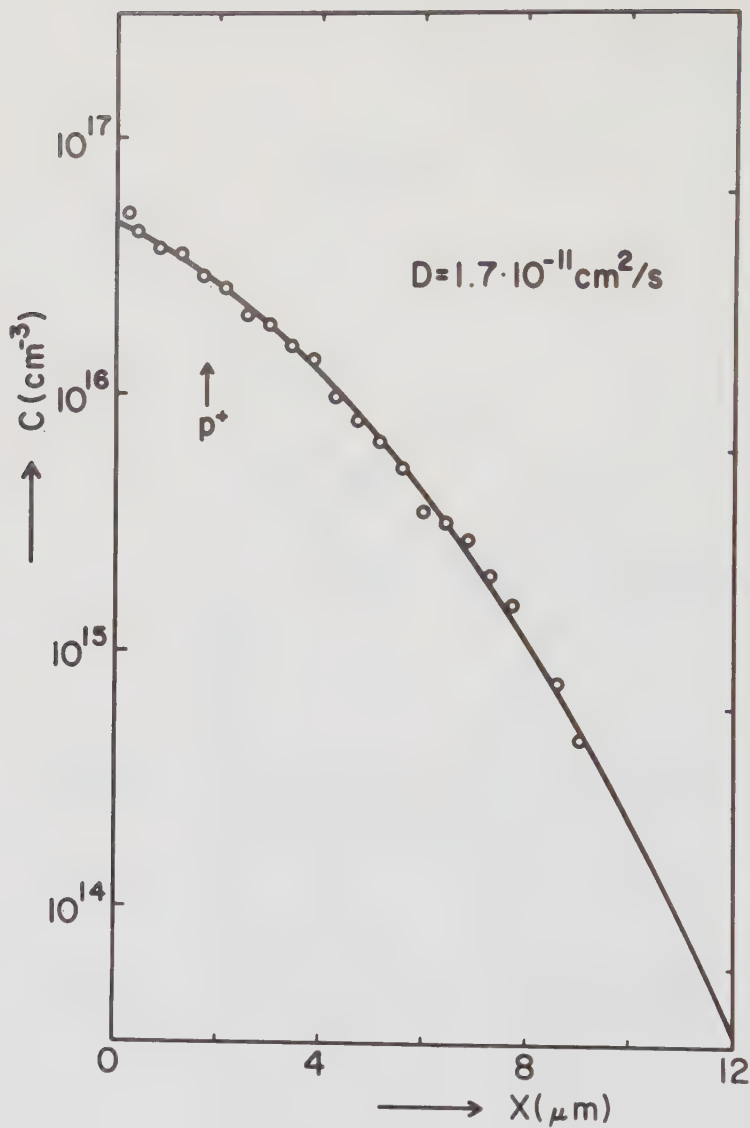


Fig.4. A SIMS profile obtained in a  $p^+n$  diode, selenium diffused for  $960^\circ\text{C}$ . The arrow indicates the beginning of the n-region. It should be noted that the error in the concentration calibration obtained by SIMS can be about one order of magnitude.

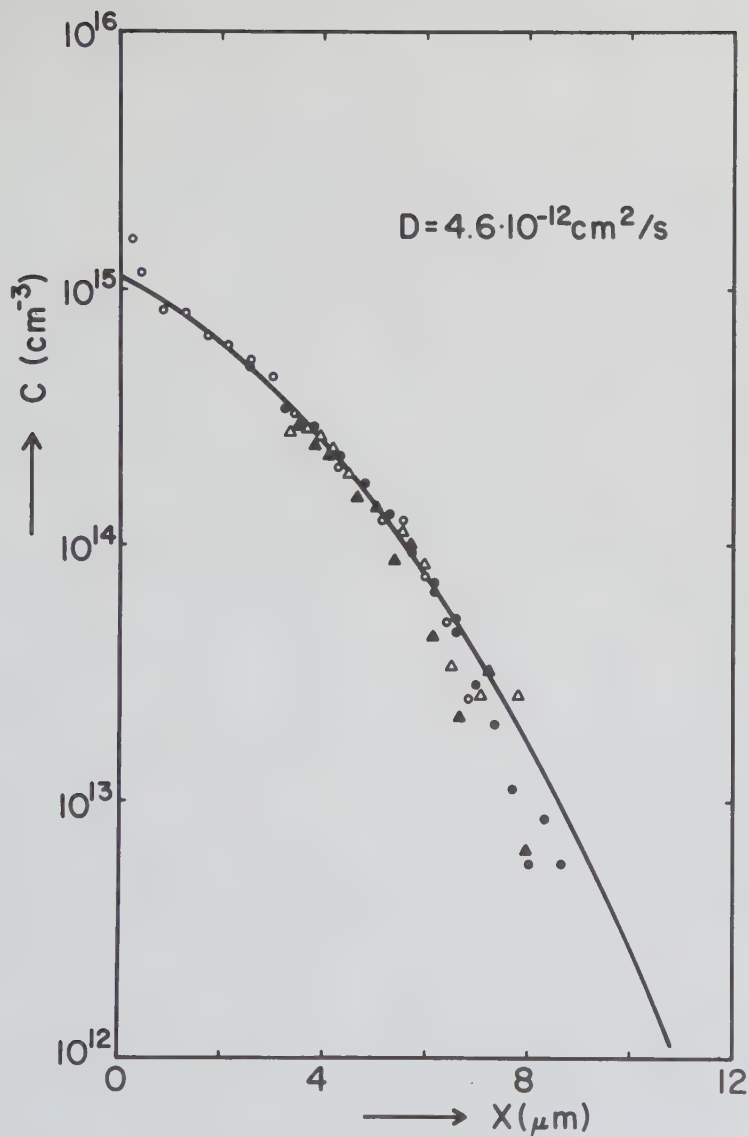


Fig.5. Diffusion profile obtained with different measuring techniques in a  $p^+n$  diode, selenium diffused for 3 1/4 h at  $900^\circ \text{C}$ .  $\Delta$ : CCS 0.57 eV center;  $\blacktriangle$ : CCS 0.30 eV center;  $\circ$ : SIMS;  $\bullet$ : DLTS 0.57 eV center. The SIMS data are shifted in concentration to fit the capacitance data.

Table I

Diffusion coefficients for selenium in silicon at four temperatures obtained with three different methods. Previously published data are shown for comparison. The 960 °C data without star are obtained from samples which have been diffused for 1 h, those with one star (\*) for 1/2 h and those with two stars (\*\*) for 2 hrs.

| T<br>(°C) | D<br>(10 <sup>12</sup> cm <sup>2</sup> /s) |        |      |        |        |        |
|-----------|--------------------------------------------|--------|------|--------|--------|--------|
|           | DLTS                                       | C - C  | SIMS | Ref.14 | Ref.15 | Ref.16 |
| 900       | 4.70                                       | 5.09   | 4.60 | 4.4    | 6.4    | 1.5    |
| 960       | 13.9                                       | 12.8   | 17.5 | 14     | 22     | 6.1    |
|           | 12.7*                                      | 10.8** |      |        |        |        |
| 1000      |                                            |        | 37.7 | 29     | 48     | 14     |
| 1050      |                                            |        | 72.9 | 66     | 120    | 37     |





Capture, emission and recombination at a deep level via an excited state.

by

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Abstract

A model of a deep trap in which the processes of carrier capture, emission and recombination go via an excited state is used to study their kinetics. It is shown that non-exponential transients can result and that detailed balance interpretations should be used with care. The model is used to interpret experiments on Si:Se and Si:S.

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## 1. Introduction

Carrier capture via an excited state into the ground state of a deep trap has been proposed as an explanation (Gibb et al, 1977, referred to as I) for a cross section which increases with temperature<sup>1</sup>. In this two step model a carrier is first captured into the excited state and the subsequent transition to the ground state goes in competition with thermal re-emission back to the band. It was argued in I that the overall capture cross-section into the ground state is reduced from that into the excited state by the branching ratio for the two possible subsequent processes. Similar arguments were applied to the process of thermal emission from the ground state and it was shown how application of detailed balance arguments to measured rates and their temperature dependences could be used to reveal the energy levels of the trap.

In fact these arguments are deceptively simple. A carrier becomes captured once it enters the excited state and a capacitance transient experiment, for example, which measures the charge state of the trap, will not distinguish between the states of excitation of a trapped carrier. Moreover a proper analysis of this two step model involves

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<sup>1</sup> Excited states of deep traps have been observed in several cases, see Grimmeiss and Skarstam (1980c), Ho and Ramdas (1972), Dean and Henry (1968) and Monemar et al, to be published.

the solution of coupled rate equations, such as have been considered elsewhere (e.g. Pickin, 1978 and references therein) and new features emerge from this analysis.

In this note we consider the consequences of the two-step model for the capture, emission and recombination transients applying the analysis to electron traps in Si:Se and Si:S. We discuss under what conditions the results of I are approximately correct and we also make qualitative predictions about the shape of transients for traps with more excited states.

In section 2 we set out the rate equations necessary for describing transient and steady state behaviour within our two step model. Section 3 describes the time dependence of capture and emission transients and section 4 discusses how the internal rates and energy levels are related to the observed transients. Section 5 considers special cases in which the transient behaviour simplifies and uses the theory to interpret data. Section 6 discusses the results of the model for steady state and transient recombination. Conclusions are drawn in section 7.

## 2. Rate equations

For definiteness we consider the traffic of electrons between the conduction band, whose edge lies at energy  $E_C$ , and a trap with an excited state at  $E_C - E_1$  and a ground state at  $E_C - E_1 - E_2$  (Fig. 1).

When the electron is in the excited or ground states we suppose the degeneracy of the system is  $g_x^*$  or  $g_g^*$  and when the electron is absent the system is  $g_0^*$ -fold degenerate. The equilibrium occupation probabilities of the ground and excited states are then given by (Landsberg, 1956).



$$f_g^0 = 1 / [1 + 1/g_g \exp [(E_c - E_1 - E_2 - \mu)/kT] + g_x/g_g \exp (-E_2/kT)] \quad (1a)$$

$$f_x^0 = 1 / [1 + g_g/g_x \exp (E_2/kT) + 1/g_x \exp [(E_c - E_1 - \mu)/kT]] \quad (1b)$$

where  $g_g = g_g^*/g_0^*$  and  $g_x = g_x^*/g_0^*$  are the degeneracies of the ground and excited states relative to the degeneracy when the electron is absent.

Capture into the excited state is described by a cross-section  $\sigma_0$ . Thus free carriers of density  $n$  and velocity  $v$  are captured into the excited states of empty traps at a rate  $v_1 = n\sigma_0 v$ . Traps in the excited state collapse into the ground state at a rate  $v_2$ .  $e_1$  and  $e_2$  are the inverse thermal re-emission rates for these processes. If we ignore direct traffic between the band and the ground state then the transient free electron concentration and occupation probabilities of traps in excited and ground states are described by

$$dn/dt = -v_1 f_0 N_T + e_1 f_x N_T + G \quad (2a)$$

$$df_x/dt = v_1 f_0 - e_1 f_2 - v_2 f_x + e_2 f_g \quad (2b)$$

$$df_g/dt = v_2 f_x - e_2 f_g \quad (2c)$$

$$\text{where } f_0 = 1 - f_x - f_g \quad (2d)$$

is the probability of finding a trap empty.  $G$  is the rate at which electrons are generated in the band by external means and  $N_T$  is the density of traps. In equilibrium the time derivatives of equations (2) are zero,  $G$  is absent and substitution of the equilibrium occupation probabilities (equation 1) provides the detailed balance relations between the  $e$  and  $v$ :

$$e_1 = 1/g_x \sigma_0 v N_c \exp (-E_1/kT) \quad (3a)$$

$$e_2 = g_x/g_g v_2 \exp (-E_2/kT) \quad (3b)$$

where  $N_c$  is the effective density of states in the conduction band.

### 3. Transient capture and emission

Capture and emission transients can be measured, for example, by using the transient capacitance technique (Grimmeiss, 1977, and Miller et al, 1977) in which the concentration of free carriers is held constant. During thermal emission free carriers are swept out by the depletion layer field so that  $n=0$ . During capture  $n$  is held fixed at the free carrier concentration in the neutral material, provided the concentration of deep traps is much smaller than  $n$  (majority capture), or at some level determined by the diffusion of optically generated free carriers from the neutral material (minority capture, Hamilton, 1974). In either case equation (2a) becomes

$$n = \text{const} \quad (2a')$$

The transient occupations are then found by solving equations 2 which reduce to a single, second order differential equation for either  $f_x$  or  $f_g$ . Both  $f_x$  and  $f_g$  show biexponential behaviour:

$$f_x(t) = \alpha \exp(m_+ t) + \beta \exp(m_- t) + C_x \quad (4a)$$

$$f_g(t) = \gamma \exp(m_+ t) + \delta \exp(m_- t) + C_g \quad (4b)$$

where the slow and fast transient decay constants,  $m_{\pm}$ , depend on the microscopic rates,  $e$  and  $v$ , and the coefficients depend in addition on the initial conditions. Details are shown in the appendix. The total occupation probability,  $f_x + f_g$  also shows biexponential behaviour.

In some cases the trap parameters may be such that either the amplitude of one of the exponentials is negligibly small or the time scales of the two exponentials are so disparate as not to be measurable in the

same experiment. Examples of such behaviour are discussed in section 5.

That this is not necessarily always so is seen from figure 2, which shows the capture transient, at various temperatures, for a trap whose parameters are given in the figure caption. The parameters are chosen to be physically reasonable and the two components of the biexponential can be seen clearly.

To observe similar behaviour in the emission transient it is necessary for the ground and excited states to lie closer than a few  $kT$  (section 5) and whilst this is not inconceivable it seems unlikely for a deep trap whose excited states result from an attractive Coulombic potential.

#### 4. Detailed balance deductions from occupation transients

For a simple trap with a single non-degenerate bound state the binding energy  $\Delta E$  can be deduced from the capture and emission decay constants,  $m_c$  and  $m_e$ :

$$\Delta E = -kT \ln \left( \frac{n}{N_c} \cdot \frac{m_e}{m_c - m_e} \right) \quad (5)$$

For a trap with biexponential capture and emission behaviour, the corresponding relations are more complex and are given in the appendix. Where only one of the exponentials is observed in capture and emission application of equation (5) to the observed exponentials may give misleading results.

## 5. Simplifications and comparison with experiment

Strong inequalities between the microscopic rates  $e$  and  $v$  can simplify transient behaviour. It may happen that the amplitude of one of the exponentials is negligibly small or that the time-scales differ widely. Sometimes the behaviour can approximate that predicted in I.

Consider a deep level such that  $E_2$  is equal to several  $kT$  (figure 1). For reasonable values of degeneracy factors it follows from equation 3b that  $e_2 \ll v_2$ . The occupation transient for thermal emission then simplifies to

$$f_x + f_g = f_g^0 \exp(m_+ t) + f_g^0 \frac{e_2}{v_2} \left( \frac{e_1}{e_1 + v_2} \right)^2 \exp(m_- t) \quad (6a)$$

where the slow and fast transients are given by

$$m_+ = \frac{-e_1 e_2}{v_2 + e_1} \quad (6b)$$

and

$$m_- = -(e_1 + v_2) \quad (6c)$$

Because of the difference in amplitudes only the slow transient is seen and its decay constant (equation 6b) is equal to that predicted in I. At high enough temperatures such that  $e_1 \gg v_2$  equation 6b simplifies to  $m_+ = -e_2$ .

General conditions which simplify the capture transients are more difficult to determine because of the extra freedom introduced in the rate  $v_1$ . It is clearer to consider particular cases.

For example capacitance transient measurements on Si:Se (Grimmeiss et al, 1980a) and Si:S (Grimmeiss et al, 1980b) show electron emission into the conduction band at a rate given by

$$e_n^t = e_0 \exp (-E_2/kT) \quad (7)$$

where for Si:Se  $e_0 = 1.95 \cdot 10^{10} \text{ s}^{-1}$  and  $E_2 = 286 \text{ meV}$

and for Si:S  $e_0 = 2.10 \cdot 10^{10} \text{ s}^{-1}$  and  $E_2 = 302 \text{ meV}$

(Fig. 3). The capture cross sections of the same traps in the range  $100 \text{ K} < T < 225 \text{ K}$  show a temperature dependence.

$$\sigma_n^t = \sigma^* T^{-2} \exp (E_1/kT) \quad (8)$$

where  $\sigma^* = 5.86 \cdot 10^{-12} \text{ cm}^2 \text{ K}^2$  and  $E_1 = 14 \text{ meV}$  for selenium  $\sigma^* = 2.94 \cdot 10^{-12} \text{ cm}^2 \text{ K}^2$  and  $E_1 = 17 \text{ meV}$  for sulphur (Fig. 4). It is tempting to interpret this behaviour in terms of a two-step capture and emission model with the measured energies ascribed to the levels as in Fig. 1<sup>1</sup>. Grimmeiss et al (1980 a and b) compare the values of  $E_1$  with the energy of the  $2p_0$  state of shallow donors in silicon, which should be the lowest state accessible by cascade capture. Both effective mass theory and experiments yield a value of 11 meV (Aggarwal and Ramdas, 1965) below the conduction band for the position of the  $2p_0$  level in reasonable agreement with the data presented above. If we ignore degeneracy factors and any temperature dependence of energy levels, set  $v_2 = e_0$  (c.f. (3b) and the high temperature limit of equation (6b)) and if we assume a capture cross section into the shallow level of no less than  $10^{-13} \text{ cm}^2$  then it turns out that only the slow transient has an appreciable

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<sup>1</sup>The existence of excited states is confirmed by photocapacitance experiments although the  $E_1$  state is too close to the conduction band to be observed in a photoionization spectrum.

amplitude and the associated rate is

$$m_+ = -\frac{v_1 v_2}{e_1} = -\frac{nv_2}{N_c} \exp(E_1/kT) \quad (9)$$

which, for a single level trap, would be interpreted in terms of a capture cross section

$$\sigma_T = \frac{v_2}{N_c v} \exp(E_1/kT) \quad (10)$$

Using the conduction band parameters for Si (Barber, 1967) this can be written

$$\sigma_T = 5.32 \cdot 10^{-12} T^{-2} \exp(E_1/kT) \quad (11)$$

for Si:Se and

$$\sigma_T = 5.72 \cdot 10^{-12} T^{-2} \exp(E_1/kT) \quad (12)$$

for Si:s. We note that the prefactors in equations (11) and (12) were derived by assuming a two step capture process and using the measured thermal emission rates (Eq.(7)). Considering the simplicity of our assumptions, which ignored degeneracy and the temperature dependence of energy levels, the agreement with direct measurement (Eq.(8)) is satisfactory.

## 6. Recombination kinetics

When recombination takes place through the trap we may allow for majority hole capture by adding further terms to equations (2b) and (2c). For simplicity, however, we make the reasonable assumptions that hole capture and emission are only significant to and from the ground

state of the trap and further that majority hole capture is so fast that the ground state is always empty. Equation (2c) then becomes

$$f_g = 0 \quad (2c')$$

Two types of recombination conditions are of interest:

1. In the steady state electrons are generated e.g. by minority injection, to balance the loss by recombination. The time derivatives on the left of equations 2 are zero and electrons are lost through traps at a rate

$$G = n \sigma_0 v N_T v_2 / (e_1 + v_2 + n \sigma_0 v)$$

which, for a single level trap, would be interpreted in terms of a total capture cross section  $\sigma_T = \sigma_0 v_2 / (e_1 + v_2 + n \sigma_0 v)$ .

At low levels of injection, or at high temperatures, when  $n \sigma_0 v \ll e_1 + v_2$ ,

$$\sigma_T = \sigma_0 v_2 / (e_1 + v_2)$$

as argued in I.

The conditions for this behaviour are found in the neutral region of a LED under D.C. operation where  $\sigma_T$  may describe the effective capture cross-section of a killer centre.

2. Under pulsed conditions a charge of minority electrons, generated for example by a cathode beam, is allowed to decay. The transient populations are found by solving equations (2) which, with  $G = 0 = f_g$ , reduce to

$$dn/dt = -n \sigma_0 v (N_T - N_x) + e_1 N_x$$

$$dN_x/dt = n \sigma_0 v (N_T - N_x) - e_1 N_x - v_2 N_x$$

where  $N_x = N_T f_x$  is the fraction of traps in the excited state. The full solution of these coupled, nonlinear differential equations is non-exponential and may be obtained numerically. In special cases the solutions simplify. Thus when the rate  $v_2$  is low enough, the excited state population first equilibrates with the free carrier concentration and then carriers leak away from the excited states, while the quasi-equilibrium is maintained.

If, in addition,  $e_1 \gg n\sigma_0 v$  so that the concentration of excited traps and free carriers are proportional then free carriers are lost from the band at a rate

$$-dn/dt = n \sigma_0 v N_T v_2 / (e_1 + \sigma_0 v N_T)$$

giving exponential decay with an apparent capture cross section:

$$\sigma_T = \sigma_0 v_2 / (e_1 + \sigma_0 v N_T)$$

At moderately high temperatures, when  $e_1 \gg \sigma_0 v N_T$  then  $\sigma_T$  shows the high temperature behaviour described in I.

Alternatively, when  $v_2 \gg \sigma_0 v n$ ,  $e_1$  capture into the excited state is the rate limiting step and the observed capture cross section is  $\sigma_0$ .



## 7. Conclusions

When capture and emission go via an excited state of a deep trap the associated transients contain two exponentials. In some cases only one may be observed because the other is either too fast or has too small an amplitude. The procedures for deducing the trap depth from the temperature dependence of the capture and emission transients are more complicated than for a trap with a single level. However the observation of only one exponential is no guarantee that the trap has only one level and application of the simpler analysis may be misleading. In special cases when the slow transient dominates, the transient rates may simplify to those described by Gibb et al (1977). For traps with further excited states further exponentials will appear in the transients and for a Coulombic trap, where trapping follows a Lax (1960) cascade (see also Abakumov, 1978), the transients will not be represented by a finite sum of exponentials.

Transient recombination via an excited state also involves non-exponential behaviour, with simplifications in special cases. The presence of the excited state will also alter the observed capture cross section during steady state recombination.

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## APPENDIX

### Transient capture and emission

The transient occupation probabilities during capture and emission are given by

$$f_x(t) = \alpha \exp(m_+ t) + \beta \exp(m_- t) + C_x \quad (4a)$$

$$f_g(t) = \gamma \exp(m_+ t) + \delta \exp(m_- t) + C_g \quad (4b)$$

where  $m_{\pm} = (-X \pm R)/2$ ,

$$R = (X^2 - 4Y)^{1/2},$$

$$X = v_1 + v_2 + e_1 + e_2$$

$$Y = v_1 v_2 + v_1 e_2 + e_1 e_2.$$

In addition we define the variables

$$A = - (v_1 + e_1 + v_2)$$

$$B = e_2 - v_1$$

In a capture transient the trap is initially empty so that

$$f_x(0) = 0 = f_g(0) \quad \text{whence}$$

$$C_x = e_2 v_1 / Y, \quad C_g = v_1 v_2 / Y$$

$$\alpha, \beta = - e_2 v_1 / 2Y \pm [e_2 v_1 (A + X/2) + B v_1 v_2] / YR$$

In an emission transient we suppose the traps are filled to an equilibrium population described by a Fermi level  $\mu$  then at  $t=0$   $f_x$  and  $f_g$  take their equilibrium values given by equations (1). The free carrier band is now empty so that  $v_1 = 0$ , whence

$$C_x = 0 = C_g,$$

$$\alpha_1 \beta = f_g^0 e_2 [R \pm (v_2 + e_2 - e_1)] / 2R v_2.$$

In both capture and emission  $\gamma$  and  $\delta$  are given by

$$\gamma = \alpha(m_+ - A) / B, \quad \delta = \beta(m_- - A) / B.$$

### Detailed balance deductions from occupation transients

For a two-step capture and emission process equation (4) does not apply in general. Instead we can deduce the microscopic transition rates,  $e$  and  $v$  from the measured fast and slow decay constants,  $m_{c,e \pm}$  during capture and emission as follows:

$$Y_c = m_{c+} m_{c-}; \quad Y_e = m_{e+} m_{e-}$$

$$X_c = - (m_{c+} + m_{c-}); \quad X_e = - (m_{e+} + m_{e-})$$

$$v_1 = X_c - X_e,$$

$$e_1 = X_e - (Y_c - Y_e) / v_1,$$

$$e_2 = Y_e / e_1,$$

$$v_2 = (Y_c - Y_e) / v_1 - e_2.$$

Application of the detailed balance relations (equations (3)) with knowledge of the degeneracies provides the energy levels  $E_1$  and  $E_2$ .

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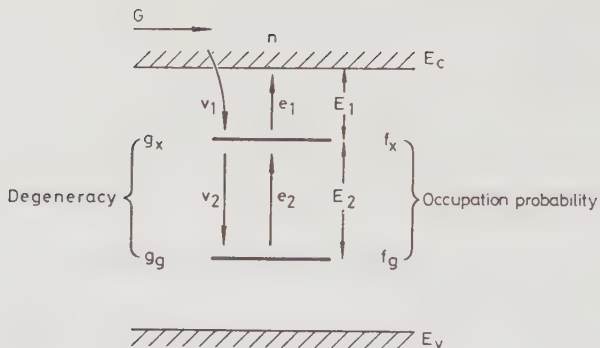


Fig.1. Energy level structure and terminology for a two level trap.

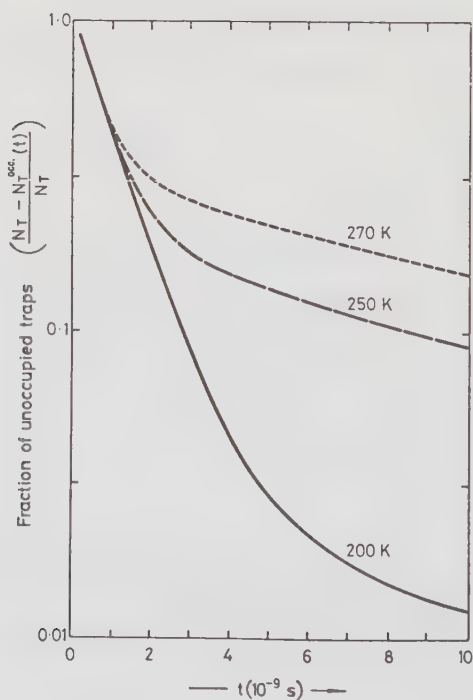


Fig.2. Capture transients at various temperatures for a trap whose parameters are  $E_1 = 150\text{meV}$ ,  $\sigma_o = 10^{-15}\text{cm}^2$ ,  $v_2 = 10^8\text{s}^{-1}$ ,  $m_n^* = 1.13m_o$ ,  $g_x = g_g = 1$  and  $E_2 = 300\text{meV}$ . The concentration of free electrons  $n$  is  $10^{17}\text{cm}^{-3}$ .

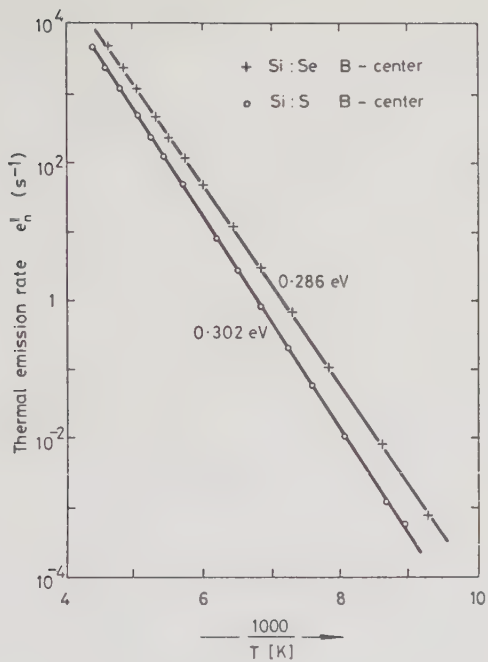


Fig.3. Electron thermal emission rates versus inverse temperature for the B-centers in Si:Se and Si:S.

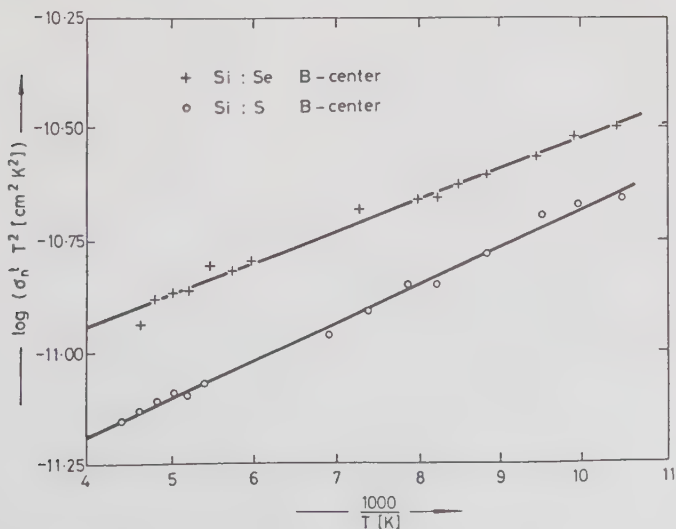


Fig.4. Temperature dependence of the electron capture cross sections for the B-centers in Si:Se and Si:S.











